crystals

MDPI

Article

Mesomorphic Investigation of Binary Mixtures of Liquid Crystal Molecules with Different Mesogenic Architectonics

Fowzia S. Alamro [1], Hoda A. Ahmed [2,*], Muna S. Khushaim [3,4], Noha S. Bedowr [5] and Nada S. Al-Kadhi [1]

[1] Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P.O. Box 84428, Riyadh 11671, Saudi Arabia; fsalamro@pnu.edu.sa (F.S.A.); nsalkadhi@pnu.edu.sa (N.S.A.-K.)
[2] Department of Chemistry, Faculty of Science, Cairo University, Cairo 12613, Egypt
[3] Department of Physics, Faculty of Science, Taibah University, P.O. Box 30002, Al-Madina 41447, Saudi Arabia; mkhushaim@taibahu.edu.sa
[4] Strategic Research Labs, Taibah University, P.O. Box 30002, Al-Madina 41447, Saudi Arabia
[5] Chemistry Department, College of Sciences, Taibah University, Yanbu 30799, Saudi Arabia; nbedowr@taibahu.edu.sa
* Correspondence: ahoda@sci.cu.edu.eg

Abstract: Different binary phase diagrams, made from two differently substituted three-rings azo/ester and azomethine/ester compounds of the same terminal alkoxy side chain of six carbons, as opposed to the other terminal polar substituent, which can either donate electrons or withdraw electrons including H. The thermal behavior of the prepared derivatives was investigated by differential scanning calorimetry and phases identified by polarized optical microscope. The first group of the binary mixtures was made from laterally F-substituted azo/ester derivatives and their laterally neat analogues. The second group of binary mixtures was made from laterally methoxy-substituted azomethine/ester derivatives and their laterally neat analogues. The final type of investigated phase diagrams was made from the laterally substituted azo and azomethine components bearing different lateral polar groups and different mesogenic moieties. Results were reviewed using phase diagrams that were produced and it was found that different mesomorphic characteristics were seen to depend on the mesogenic component as well as lateral and terminal polar groups. In all cases, these mixtures have been determined to have low melting-temperature eutectic compositions, while linear or negative deviation of nematic or smectic isotropic composition temperature dependence was observed.

Keywords: liquid crystal mixtures; binary phase diagrams; lateral substitution; eutectic composition; thermal characterizations

check for updates

Citation: Alamro, F.S.; Ahmed, H.A.; Khushaim, M.S.; Bedowr, N.S.; Al-Kadhi, N.S. Mesomorphic Investigation of Binary Mixtures of Liquid Crystal Molecules with Different Mesogenic Architectonics. *Crystals* **2023**, *13*, 899. https://doi.org/10.3390/cryst13060899

Academic Editor: Mingjun Huang

Received: 28 April 2023
Revised: 24 May 2023
Accepted: 29 May 2023
Published: 31 May 2023

1. Introduction

Liquid crystal mixtures are of great theoretical and practical interest. The phase behavior of these mixtures is far more complex compared with that of isotropic fluid mixtures, thus display systems generally use mixtures whose physical features are better suited for device applications than those of pure materials [1–3]. Liquid crystals' (LCs) electro optical response is greatly influenced by rotational viscosity, dielectric characteristics, and birefringence [4–7]. A specific set of desired physical properties is needed depending on their uses. Since no single compound may have all the required features, it is typical to mix different types of liquid crystals in predetermined quantities to adjust the physical characteristics for commercial devices. Moreover, research on liquid crystal mixes with a range of forms and architectures has consistently shown to be fruitful from both a technological and fundamental point of view.

There have been identified a number of novel phases that are not found in the parent compounds [8–10]. Binary mixtures of symmetric and non-symmetric molecules, such as those made up of mixtures of molecules with rod-like and bent shapes, have led to the development of various new physical features [11–15]. Nevertheless, physical research on binary nematic liquid crystal mixtures bearing similar core structures and strongly antagonistic dipole orientation is few. It is well known that molecules with high dipole moments contribute significantly to intermolecular interactions which provide different physical features in liquid crystals [11–15].

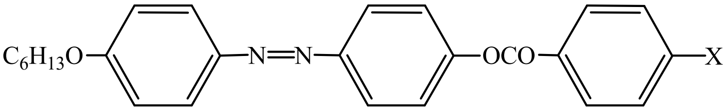
In the development, nature, thermal stability, and LC temperature mesophase ranges, the central bridges, terminal side groups, and molecular shapes all play key roles, which has been reported [16–31]. Goodby and colleagues also described how the mesophases of the LCs can be affected by reducing free volume of the system; examples include (a) smectic A phases with variable layer spacing, (b) smectic C phases without layer shrinkage, and (c) lattices of empty space and fibers in the twist-bend N phase [32].

When a lateral group is added to a nematic core, the physical characteristics of liquid crystalline mesogens are significantly altered. The lateral substituent efficiently widens the core in terms of the steric effect, which raises intermolecular separation. As a result, the lateral alignments of the rod-shaped molecules are diminished, which lowers their mesophase stability [33–43]. A lateral methyl substituent has been discovered to significantly lower melting points and N stability. On the other hand, as the terminal alkyl chain lengthens, it adopts the conformation that follows the mesogenic core. As a result, neither the melting temperatures nor the N stability are significantly depressed [44]. In general, compact, polar, and polarizable groups (as F and CH_3O) appear to be extremely effective at producing high clearing points. The clearing point appears to fall when the group's polarity does as well. These researchers explained this by noting that as the polarity and polarizability of the substituent grow, so do the intermolecular attractions [44–46].

In a recent study [45] conducted in our lab, the mesophase behavior of compounds of the type 4-(4′-hexyloxy phenylazo) phenyl 4″-substituted benzoates (**I6**$_{\mathbf{a–c}}$) was examined in relation to the effects of a small, compact terminal polar substituent, X, and terminal alkoxy groups of varied chain length. In that study [45], it was found that the polarity and/or polarizability of the mesogenic molecular part, which is strongly influenced by its polarity, location, or orientation and would consequently impact the polarity of the entire molecular architecture by the way the polar moiety interacts mesomerically with the rest of the molecule, leads to the increase of the stability of the mesophase.

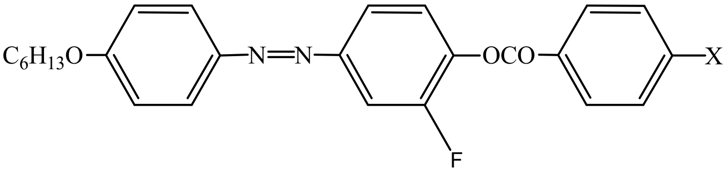
Specific liquid crystal derivatives were developed in order to produce phase diagram mixes. This was performed for two reasons: first, they can create LC mesophases when mixed together, and second, they recently showed that when mixed with mesomorphic materials, they drastically change the phase behavior of LCs material [44–46].

Due to the great capabilities in the area of optical-communication and potential to support computing methods for the advancement of signal processing in all-optical data networks in the future, optical logic components have garnered a lot of interest [46]. Optical fibers, semiconductor optical amplifiers, and photonic crystals (PC) are just a few of the materials and technologies that have been employed to create all-optical logic gates [47]. Due to their intriguing physics and potential for technological innovation, liquid crystal mixtures have been the subject of extensive research. High mesogen concentrations can cause mixtures to remain homogeneous and behave almost exactly like pure materials, but they can also cause mixtures to phase-separate, creating heterogeneous materials with intricate morphologies and order parameter gradients that can significantly alter and enhance a material's properties. It is preferable for practical studies that LC derivatives exhibit their transitions at room temperature and maintain their mesomorphic nature over a large temperature range. When different components are combined, mesomorphic requirements of mesogenic cores are significantly altered. Using mixtures is one approach to do this because, in such cases, the mesophase-isotropic transition is linearly varied or somewhat improved with composition [48–51]. Furthermore, compared to either of its two pure components, the minimal-melting eutectic mixture has a greater mesophase temperature range. The purpose of the current work is to examine first the impact of adding a lateral F atom (**II6**$_{\mathbf{a–e}}$) [52] on azo/ester laterally neat derivatives (**I6**$_{\mathbf{a–e}}$) on each particular compound's binary mesophase behavior. Secondly, to study the mesophase behavior of binary mixtures generated from any two analogues from the laterally methoxy azomethine/ester components with their laterally neat analogues (**III6**$_{\mathbf{c,e}}$ and **IV6**$_{\mathbf{a–e}}$) [53,54]. Thirdly, to investigate the binary mixtures produced from the laterally substituted azo/ester and azomethine/ester derivatives to evaluate the effect of different mesogenic part on the mesomorphic binary phase diagram properties. The study seemed to be sufficiently confined to the one extreme homologues with n = 6 carbons (See Figure 1).



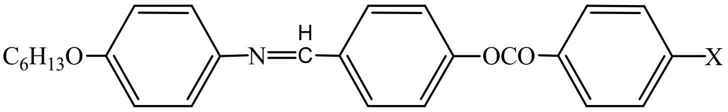
I6$_{\mathbf{a-c}}$

a, X = MeO; b, X = Me; c, X = H



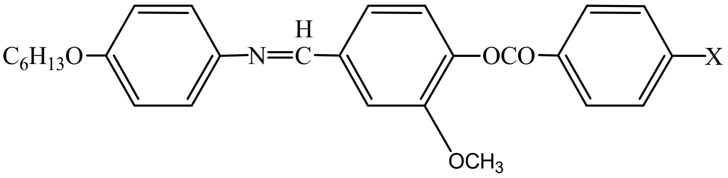
II6$_{\mathbf{a-e}}$

a, X = MeO; b, X = Me; c, X = H; d, X = Cl; and e. X = F



III6$_{\mathbf{c,e}}$

c, X = H and e. X = F



IV6$_{\mathbf{a-e}}$

a, X = MeO; b, X = Me; c, X = H; d, X = Cl; and e. X = F

Figure 1. Molecular structures of the investigated compounds.

2. Results and Discussion

2.1. Mesophase Behavior of Pure Materials

Transition temperatures for the investigated three-ring compounds (**I6**$_{\mathbf{a–c}}$, **II6**$_{\mathbf{a–e}}$, **III6**$_{\mathbf{c,e}}$, **IV6**$_{\mathbf{a–e}}$) that differ in one of their liking groups (azo and azomethine) are prepared as given in previous investigations [45,52–54], and their transition temperatures are collected in Table 1. It has been shown that molecular polarity plays a substantial role in intermolecular attractions, which are the main cause of a LC compound's mesophase stability [55] that within one series of compounds the dipole moments of its individuals is impacted by the nature of the substituents. The degree of conjugation inside the molecule impacts its ability to take on polarization, which in turn affects the resulting dipole moment. On the other hand, it has been shown [56] that, regardless of the length of the alkoxy chain, it is discovered that all members of a homologous series have dipole moments that are remarkably identical. This conclusion is supported by the fact that alkoxy groups have comparable polarity regardless of their length and thus do not alter in our groups of compounds the strength of the connection between the ester carbonyl and alkoxy oxygen, As can be seen from Table 1, the laterally neat azo/ester homologue **I6**$_{\mathbf{a–c}}$ are monomorphic possessing only the nematic mesophase enantiotropically. Both derivatives of the 4-methoxy and methyl analogues showed a broad nematogenic range with high thermal stability. However, the terminally un-substituted analogue (X = H) showed a reduced N stability and its temperature mesophase range.

Table 1. Mesomorphic transition (temperature, °C, and enthalpy, kJ/mole) for formed materials.

Comp.	X	Phase Transitions
I6a	OCH_3	Cr 107 (44.11) N 257 (2.21) I
I6b	CH_3	Cr 130 (38.18) N 215 (1.70) I
I6c	H	Cr 122 (34.41) N 161 (2.57) I
II6a	OCH_3	Cr 99 (43.12) N 186 (1.91) I
II6b	CH_3	Cr 131(48.23) N 167 (2.24) I
II6c	H	Cr 108 (55.34) I
II6d	Cl	Cr 125 (44.25) N 232 (2.11) I
II6e	F	Cr 100 (40.13) N 181 (1.52) I
III6c	H	Cr 67 (28.38) SmA 87 (1.92) I
III6e	F	Cr 74 (25.49) SmA 148 (1.81) I
IV6a	OCH_3	Cr 105 (62.51) N 156 (0.99) I
IV6b	CH_3	Cr 90 (49.71) N 141 (0.78) I
IV6c	H	Cr 99 (53.44) I
IV6d	Cl	Cr 99 (58.36) N 137 (0.64) I
IV6e	F	Cr 122 (48.50) N 117 * (0.72) * I

* Monotropic nematic phase.

In the case of lateral F substitution (**II6**$_{\mathbf{a–e}}$), the polarity of the other terminal substituent, X, as well as the orientation of the lateral F atom, determines the kind and stability of the mesophase. That is the electron-donating (MeO and Me) and the electron-withdrawing (F and Cl) substituted derivatives showed to exhibit fully the N phase thus are mesomorphic, while the un-substituted derivative (**II6**$_{\mathbf{c}}$) is totally non-mesomorphic. Hence, the mesophase has been produced by the addition of a terminal polar group to the mesogenic molecular structure. The shape of the molecule, polarity of the linked groups, aspect ratio, polarizability, molecular rigidity, and polarizability are generally considered to be important variables that affect the thermal stability, mesophase range, and texture types of the produced mesophases. Thus, comparing series **I** with **II**, the introduction of the lateral fluorine atom into the central ring ortho to the ester oxygen has led to the decrease of the nematic stability due to its steric hindrance that affects the alignment of adjacent molecules.

On the other hand, the laterally neat azomethine/ester analogues, **III6**$_{\mathbf{c,e}}$ were found to be smectogenic exhibiting the smectic A phase enantiotropically. The incorporation of the electron-withdrawing halogens (X = F) enhances the mesophase stability compared to its un-substituted derivative. Furthermore, the replacement of azo linkage by an azomethine connecting bridge influences the mesomorphic characteristics that lead to formation of the smectic A (SmA) phase in **III6$_c$** derivative. Finally, in the 4-(((4-(hexyloxy)phenyl)imino)methyl)-3-methoxyphenyl 4-substituted benzoates (**IV6$_{a–e}$**) bearing the lateral CH_3O group attached to the central benzene ring, except for the terminally un-substituted derivative (**I6$_c$**, X = H), all produced derivatives are mesomorphic in nature with a mesomorphic range and their stability is dependent on the polarity of their terminal substituent. Moreover, each compound is monomorphic, only having the nematic phase. In the following order, the mesomorphic range and stability decreases in the order: $CH_3O > CH_3 > Cl > F > H$. For compounds **IV6$_{a,b}$**, the enantiotropic nematic phase was formed with highest nematic stability and temperature ranges. However, the compounds having the electron-withdrawing groups (X = Cl and F) possess less thermal stability. For compound **IV6$_d$** (X = Cl), it exhibits the enantiotropic N phase. For the terminally substituted fluoro derivative (**IV6$_e$**), the compound is purely nematogenic; however, it exhibits the monotropic N phase with minimum range of thermal stability. In the case of un-substituted derivative (**IV6$_c$**), it is non-mesomorphic.

In general, the mesophase interaction of a particular calamitic mesogen is directly influenced by molecular–molecular associations as well as the stereo and/or mesomeric characteristics of the molecule. Three interfering factors primarily impact the molecular interactions of the calmitic structures in the present compounds and, consequently, their phase stability (TC), whether in their pure or mixing states:

1. As the alkoxy-chain length (n) rises, there is an increase in the lateral adhesion between linear molecules.
2. Different mesomeric effects result from an end-to-end association that changes depending on the polar terminal moiety, which in turn results in different dipole-dipole interactions.
3. It was found that the lateral methoxy substituents' steric influence varied depending on their position and, subsequently, their orientation.
4. The molecule's molecular structure affects the mesophase structure.

The mesophase behavior of the diverse binary mixes under investigation is affected by these four elements in varying proportions.

2.2. Mesophase Behavior of Binary Phase Diagrams

Binary systems have frequently been employed, resulting in liquid crystalline phases over a wide temperature range. The parallel molecular arrangement required for the creation of liquid crystal phases becomes obvious if an electron donor–acceptor charge transfer interaction serves as the orientational forces in binary mixtures of electron donors and electron acceptors [57,58]. In the binary phase system of butylaniline and pentylbiphenyl derivatives, where a mild charge transfer interaction within molecules takes place between the donor and the acceptor, Park et al. [58] investigated the N-isotropic phase temperature ($T_{N\text{-}I}$). Even though the nematic phase is present in both components of the mixture in this example, the composition dependency of $T_{N\text{-}I}$ showed a broad curve with a maximum close to the 1:1 molar ratio, and its $T_{N\text{-}I}$ was found to be higher than that predicted from the straight line connecting the $T_{N\text{-}I}$ of the two components.

Even when both components of a binary mixture of donors and acceptors are non-mesomorphic, the mixture occasionally turned out to be potentially mesomorphic. By observing nematic phase in binary combinations of possibly mesomorphic electron donors and acceptors of type N-(4-X-benzylidene)-4′-Y-aniline, this was accomplished by Araya and Matsunage [58]. If the terminal X or Y substituents is a dimethyl amino group, it functions as a donor; if X or Y is a nitro group, it functions as an acceptor.

Another study [59] investigated chemicals that are neither nor both mesogens could be combined to produce mixed mesomorphism. Significant attention has been given to the mesophase's generation [60], changes in mixed mesomorphic ranges and thermal stabilities, and analyses of the variables that affect alterations. Moreover, combinations of two non-LC components have been observed to exhibit liquid crystallinity. For instance, according to Mlodziejowski [61], combining molten cholesterol with cetyl alcohol or glycerol resulted in mesomorphic phase formation. Earlier, Gaubert [62] reported that combining molten cholesterol with succinimide and acids will result in mesomorphic systems. Gaubert also focused on the liquid crystalline combinations produced when ergosteryl acetate, propionate, or butyrate was heated in the presence of glycolic acid, glycerol, and orcin, as well as the mesomorphic mixtures produced by melting a few derivatives of ergosterol and cholesterol with urea. Kravchenko and Pastukhova [63] have also reported on phase characteristics for mixtures of non-liquid crystal materials, such as the hydrocarbons indene and naphthalene. Dave et al. [64] examined the influence of mixed mesophase that comes from these differences by contrasting the phase behavior of four binary phase diagrams made up of structurally related mesogenic parts and a terminal moiety that contains nematogens. The binary mixtures under examination were mesomorphic azo and esters derivatives. The analysis of these binary systems revealed that the N-I, SmA-N, and SmA-I curves differ from linearity as the molecular geometry of the two components in the binary mixture varies. There are a number of moieties that make up the central bridges and terminal groups to contribute to this non-linear tendency. When one of the two components of the binary mixture has a strong polar end group, some studies have demonstrated the non-linear interaction of binary phase diagrams [65–67]. The reason for the divergence from linearity was determined to be the nitro group's strong inclination to promote the development of orientated fluids in these binary systems.

Saad and Nessim [68] examined new model materials in order to evaluate the impact of the terminal alkoxy moiety on the stability of the mesophase interaction in their pure states as well as in their binary mixes with each other and with their NO_2 analogue in an investigation into the impact of molecular structural length on the phase behavior of some liquid crystal materials and their binary phase mixtures. No significant variations in the eutectic mixtures' mesophase stability or mode of phase behavior were found in the C_{12}–C_{20} range under study. The eutectic composition, which varies depending on the lengths of the chains connected to both components of the mixture, was the only effect seen.

Ahmed et al. [69–72] also investigated new liquid crystalline binary mixtures with different geometrical structures. It was found that the type and thermal stability of binary mixtures are mainly dependent on the mesomeric interactions between molecules according to the polarity of attached substituents. Moreover, most of the binary systems showed depression in melting transition temperatures.

2.2.1. Binary Mesophase Behavior of the Laterally F-Substituted Azo/Ester Derivatives with Their Laterally Neat Series

Three sample examples of binary mixtures between laterally neat analogue (**I6**$_{\mathbf{a–c}}$) and its laterally F-substituted analogue (**II6**$_{\mathbf{a–c}}$) are shown in Figure 2; components of the mixtures are made of various terminal polar groups (X). Figure 2a shows that the melting temperature decreased when the **I6**$_{\mathbf{a}}$ was added to the laterally F analogue (**II6**$_{\mathbf{a}}$), both of which possessed similar alkoxy chain length of six carbons. The negative slope of the stability of the nematic phase indicates that the steric effect of the lateral flouro group as it affects the pure component **II6** also affects its binary mixtures with the laterally neat analogues **I6**. The negative effect depends on the polarity of the terminal moiety X, where the slope of the linear dependence varies with X. This system's eutectic mixture, which contains about 60 mol% **II6**$_{\mathbf{a}}$, has a broad nematic temperature range of 132 °C, although its nematic stability varies often and slightly with composition. This behavior indicates that the molecules of the two components display almost ideal nematic arrangements, which is supported by the nearly linear dependence of $T_{N\text{-}I}$ on composition. On the other hand, for X = CH_3 (Figure 2b), the addition of nearly 20 mol% of **II6**$_{\mathbf{b}}$ to **I6**$_{\mathbf{b}}$ resulted in an eutectic temperature with nematic range and thermal stability 91 and 210 °C, respectively. For terminally neat X = H (Figure 2c), a narrow nematic range was observed in the binary phase diagram and the eutectic point formed at about 40 mol% of **II6**$_{\mathbf{c}}$. Each diagram simply displayed the nematic phase, which varies more or less linearly with composition while the eutectic mixtures melt at slightly lower temperature compared with pure components.

This result is consistent with the two derivatives having different solid-phase structures, although their mesophases are not significantly impacted by the location or orientation of the lateral F atom.

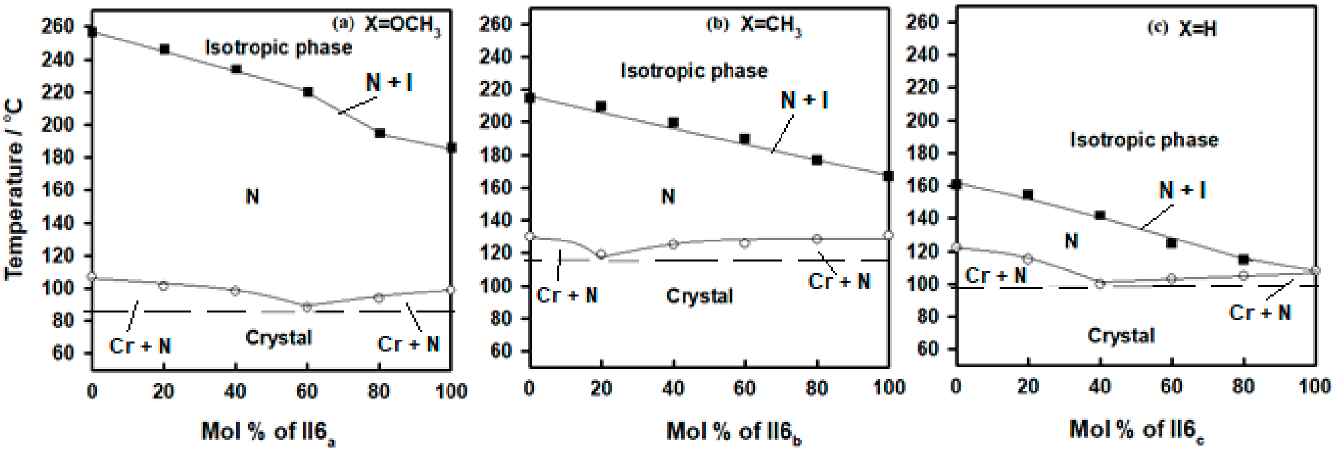


Figure 2. Systems with binary phase diagrams: (**a**) **I6$_a$/II6$_a$**, (**b**) **I6$_b$/II6$_b$**, (**c**) **I6$_c$/II6$_c$**.

2.2.2. Binary Mesophase Behavior of the Laterally CH$_3$O-Substituted Azomethine/Ester Derivatives with Their Laterally Neat Analogues

Similar to this, Figure 3 displays the binary phase diagrams of the 4-(((4-((4-(hexyloxy) phenyl)imino)methyl))-3-methoxyphenyl 4-substituted benzoates **III6$_{c,e}$** with their laterally neat azomethine/ester counterparts **IV6$_{c,e}$**. Both binary mixes demonstrated eutectic composition and decrement composition dependence of the T$_{SmA–I}$ temperatures, as shown in Figure 3. This pattern suggests that the lateral methoxy group's insertion alters the molecular configurations of the two components being combined. The addition of the component **III6$_c$** to component **IV6$_c$** is accompanied by a linear decreasing smectic behavior and the smectic A phase is totally disappeared upon addition of about 60% mole **IV6$_c$**. This system contains eutectic mixture at about 20 mol% **IV6$_c$** (Figure 3a). For the electron-withdrawing homologues (Figure 3b), the reverse holds good; that is the smectic A phase of the **III6$_e$** is totally covering the whole compositions range of **IV6$_e$**.

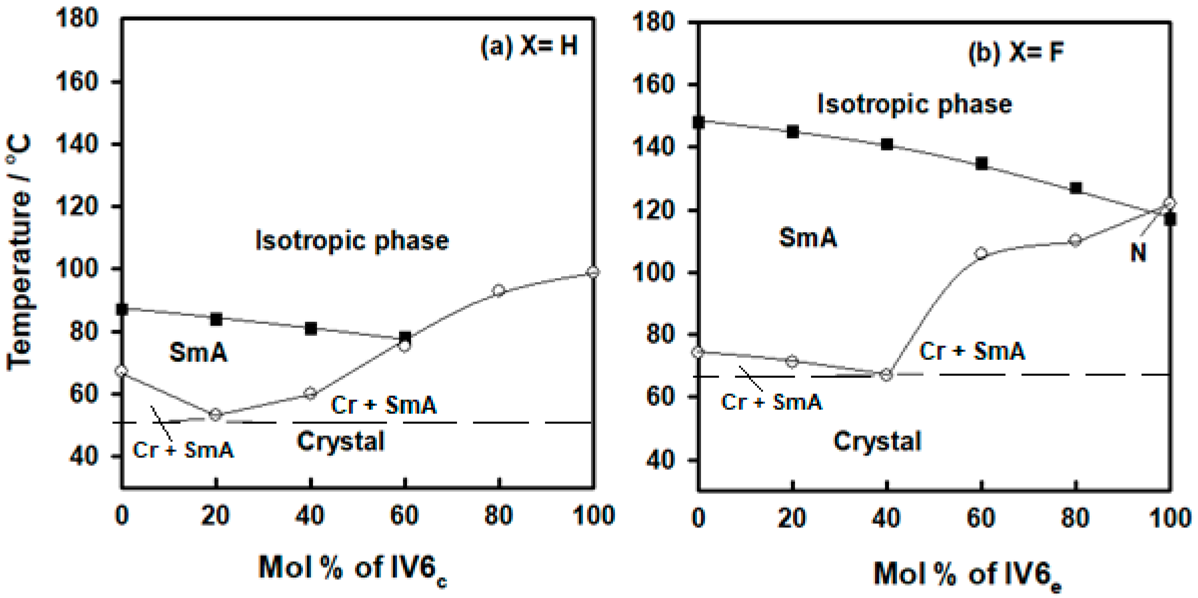


Figure 3. Systems with binary phase diagrams: (**a**) **III6$_c$/IV6$_c$**, (**b**) **III6$_e$/IV6$_e$**.

2.2.3. Binary Mesophase Behavior of Two Different Laterally Substituted Derivatives with Different Linkages

Figure 4 shows the systems with binary phase diagrams made for the binary combinations produced from the laterally F-substituted azo/ester derivatives (**II6$_{a–e}$**) and laterally OCH$_3$-substituted/ester components (**IV6$_{a–e}$**), respectively. While their Cr-N transition temperatures pass through eutectic mixtures, all diagrams for the four systems under study only showed the nematic phase, which varies more or less linearly with composition. This behavior is in line with the fact that the two components have different solid phase structures, whereas the different lateral groups or the linking azo and Schiff base connecting groups have little to no impact on the two components' mesophases.

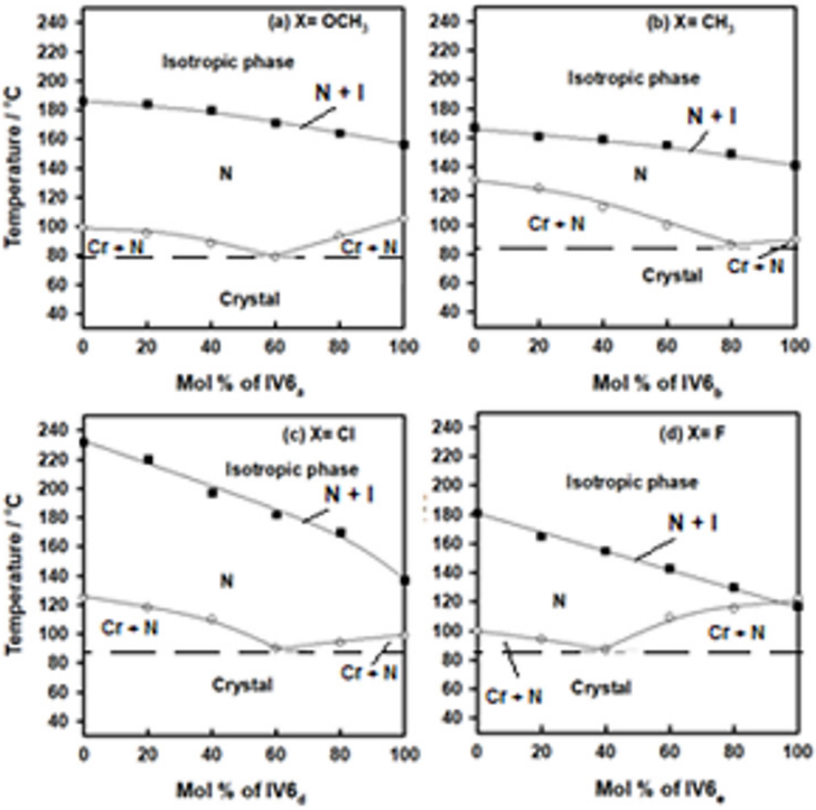


Figure 4. Systems with binary phase diagrams: (**a**) **II6$_a$/IV6$_a$**, (**b**) **II6$_b$/IV6$_b$**, (**c**) **II6$_d$/IV6$_d$**, (**d**) **II6$_e$/IV6$_e$**.

Figure 4a shows that the melting temperature decreases upon addition of **II6$_a$** to **IV6$_a$**, both of which possessed similar alkoxy chain length but with different lateral polar groups and different mesogenic parts. This system **II6$_a$/IV6$_a$** showed eutectic composition at about 60 mol% **II6$_a$** with a low melting transition temperature at 79 °C, although its nematic thermal stability decreases with composition. The behavior of these compounds suggests that the two constituent molecules disrupt the ideal nematic arrangements of each other due to the different structures of both components. On the other hand, for X = CH$_3$ (Figure 4b), the addition of nearly 40 mol% of **II6$_b$** to **IV6$_b$** resulted in a eutectic temperature with melting point 86 °C. Moreover, a narrow nematic range was observed in this binary phase diagram. Similar behavior has been observed in Figure 4c,d for the electron-withdrawing substituted analogues (X = Cl and F). This result is consistent with the two derivatives having different solid-phase structures, although their mesophases are significantly affected by the different mesogenic structures of both derivatives.

Representative example of DSC thermograms of 60 mol % of **II6$_a$/IV6$_a$** is presented in Figure 5 and POM nematic texture of observed mesophase is depicted in Figure 6 and Supplementary Materials.

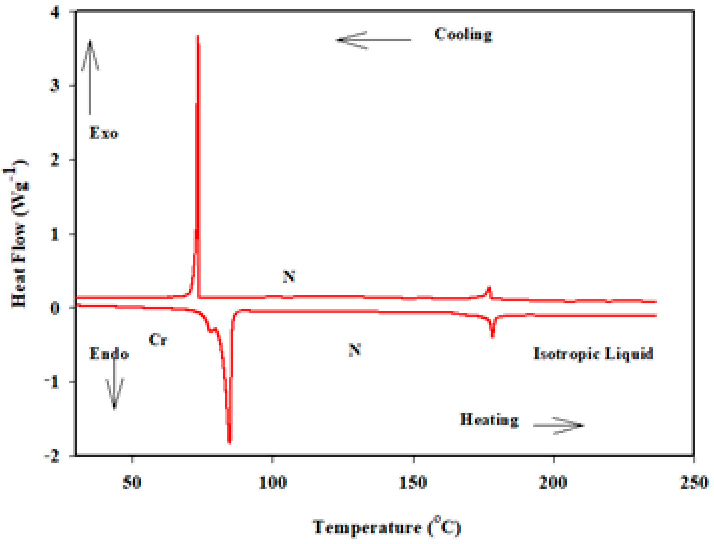


Figure 5. DSC thermogram obtained during heating of 60 mol % of **II6a/IV6a** binary mixture.

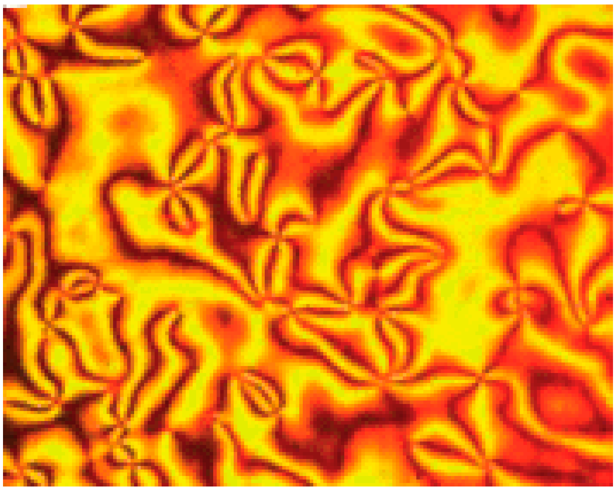


Figure 6. POM image (209 × 158 px) under crossed polarizers of the nemtic phase upon heating of 60 mol % of $\mathbf{II6_a/IV6_a}$ system at 100 °C.

3. Experimental

As previously published [45,52–54], compounds **I–IV** used in this investigation were prepared and fully characterized.

Weighed materials of the calculated quantities of each pure component (1.0% of composition) were combined, melted to form an intimate blend, and then cooled to 20 °C while being agitated in order to create binary mixtures.

4. Conclusions

We examined three different forms of binary phase diagrams, the first of which is composed of laterally flouro-substituted azo/ester derivatives and their laterally neat analogues. The second is made up of laterally neat analogues of azomethine/ester derivatives that have been laterally methoxy substituted. The third phase diagram was created between two different substances with structurally lateral substitutions and several mesogenic moieties. The molecules have different terminal polar X groups attached to one end whereas just one homologue with n = 6 carbons has been employed.

The analysis of the phase diagrams that had been prepared showed that:

1. For systems of binary phase diagrams made from laterally F- substituted azo/ester derivatives with their laterally neat compounds, all systems showed enantiotropic N mesophase, which changes more or less linearly with composition.
2. For binary systems made from laterally methoxy-substituted azomethine/ester derivatives with their laterally neat analogues, all systems showed a solid eutectic behavior associated with a linear decrement smectic A behavior. For the electron-withdrawing homologues (X = F), the SmA phase is totally covering all the compositions of $\mathbf{IV6_e}$, while for X = H, the SmA phase is destroyed upon addition of about 60% mole $\mathbf{IV6_c}$.
3. In the binary systems of the two differently laterally substituted derivatives having different linkages, the mesomorphic properties of mixtures have been affected by the different mesogenic structures of both azo and azomethine derivatives.
4. All binary mixture systems show eutectic mixtures with depression in melting transitions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst13060899/s1, Figure S1, POM image (209 × 158 px) under crossed polarizers of the nemtic phase upon heating of 20 mol % of $\mathbf{I6_a/II6_a}$ system at 200 °C; Figure S2, POM image (209 × 158 px) under crossed polarizers of the smectic A phase upon heating of 40 mol % of $\mathbf{III6_e/IV6_e}$ system at 120 °C.

Author Contributions: Conceptualization, F.S.A., N.S.A.-K. and H.A.A.; methodology, H.A.A. and M.S.K.; validation, N.S.B., F.S.A., N.S.A.-K. and M.S.K.; formal analysis, F.S.A., N.S.B. and N.S.A.-K.; and H.A.A.; investigation, F.S.A. and H.A.A.; resources, M.S.K., N.S.B., H.A.A. and N.S.A.-K.; data curation, H.A.A. and F.S.A.; writing—original draft preparation, N.S.B., F.S.A., N.S.A.-K., H.A.A. and M.S.K.; writing—review and editing, H.A.A. and F.S.A.; visualization, N.S.A.-K.; supervision, H.A.A. and F.S.A.; project administration, H.A.A. and F.S.A.; funding acquisition, F.S.A. and H.A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by "Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R107), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia".

Data Availability Statement: The data used for research described in this manuscript are available upon request from corresponding author: ahoda@sci.cu.edu.eg (H.A.A.)

Acknowledgments: The authors extend their sincere appreciation to "Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2023R107), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia".

Conflicts of Interest: The authors state that the publishing of this work does not include any conflict of interest.

References

1. Gilani, A.G.; Khoshroo, N.; Mohammadi, M.; Kula, P.; Rychłowicz, N. Optical and thermodynamic studies on binary mixtures composed of two-isothiocyanato liquid crystals. *J. Mol. Liq.* **2023**, *369*, 120925. [CrossRef]
2. Chaudhary, M.; Ghildyal, D. Investigations of axioms of twist grain boundary phases (TGBPs) in binary mixture of liquid crystals. *Int. J. Mod. Phys. B* **2023**, *37*, 2450006. [CrossRef]
3. Alhaddad, O.A.; Khushaim, M.S.; Gomha, S.M.; Ahmed, H.A.; Naoum, M.M. Mesophase behavior of four ring ester/azomethine/ester liquid crystals in pure and mixed states. *Liq. Cryst.* **2022**, *49*, 1395–1402. [CrossRef]
4. de Gennes, P.G. *The Physics of Liquid Crystals*, 2nd ed.; Clarendon: Oxford, UK, 1993.
5. Chandrasekhar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, UK, 1977.
6. de Jeu, W.H. *Physical Properties of Liquid Crystal Materials*; Gordon and Breach: New York, NY, USA, 1980.
7. Blinov, L.M.; Chigrinov, V.G. *Electrooptic Effects in Liquid Crystal Materials*; Springer: New York, NY, USA, 1994.
8. Pramod, P.A.; Pratibha, R.; Madhusudana, N.V. A three-dimensionally modulated structure in a chiral smectic-C liquid crystal. *Curr. Sci.* **1997**, *73*, 761–765.
9. Dhara, S.; Pratibha, R.; Madhusudana, N.V. Some experimental investigations on type II chiral liquid crystals. *Ferroelectrics* **2002**, *277*, 13–23. [CrossRef]
10. Pratibha, R.; Madhusudana, N.V.; Sadashiva, B.K. An orientational transition of bent-core molecules in an aniso-tropic matrix. *Science* **2000**, *288*, 2184–2187. [CrossRef]
11. Madhusudana, N. Liquid crystals made of highly polar compounds. *Braz. J. Phys.* **1998**, *28*, 301–303. [CrossRef]

12. Warrier, S.R.; Vijayaraghavan, D.; Madhusudana, N.V. Evidence for a nematic-nematic transition in thin cells of a highly polar compound. *EPL Europhys. Lett.* **1998**, *44*, 296–301. [CrossRef]
13. Prost, J.; Toner, J. Dislocation-loop melting theory of phase diagrams with nematic regions surrounded by smectic regions. *Phys. Rev. A* **1987**, *36*, 5008–5014. [CrossRef]
14. Cladis, P.E. New Liquid-Crystal Phase Diagram. *Phys. Rev. Lett.* **1975**, *35*, 48–51. [CrossRef]
15. Ananthaiah, J.; Sahoo, R.; Rasna, M.V.; Dhara, S. Rheology of nematic liquid crystals with highly polar molecules. *Phys. Rev. E* **2014**, *89*, 022510. [CrossRef] [PubMed]
16. Omar, A.Z.; El-Atawy, M.A.; Alsubaie, M.S.; Alazmi, M.L.; Ahmed, H.A.; Hamed, E.A. Synthesis and Computa-tional Investigations of New Thioether/Azomethine Liquid Crystal Derivatives. *Crystals* **2023**, *13*, 378. [CrossRef]
17. Jevtovic, V.; Ahmed, H.A.; Khan, M.T.; Al-Zahrani, S.A.; Masood, N.; Jeilani, Y.A. Preparation of Laterally Chlo-ro-Substituted Schiff Base Ester Liquid Crystals: Mesomorphic and Optical Properties. *Crystals* **2023**, *13*, 835. [CrossRef]
18. Ikeda, T. Photomodulation of liquid crystal orientations for photonic applications. *J. Mater. Chem.* **2003**, *13*, 2037–2057. [CrossRef]
19. Al-Zahrani, S.A.; Khan, M.T.; Jevtovic′, V.; Masood, N.; Jeilani, Y.A.; Ahmed, H.A. Design of Liquid Crystal Materials Based on Palmitate, Oleate, and Linoleate Derivatives for Optoelectronic Applications. *Molecules* **2023**, *28*, 1744. [CrossRef] [PubMed]
20. Blatch, A.E.; Luckhurst, G.R. The liquid crystal properties of symmetric and non-symmetric dimmers based on the azobenzene mesogenic group. *Liq. Cryst.* **2000**, *27*, 775–787. [CrossRef]
21. Thaker, B.T.; Kanojiya, J.B. Mesomorphic properties of liquid crystalline compounds with biphenyl moiety containing azo-ester, azo-cinnamate linkages and different terminal group. *Liq. Cryst.* **2011**, *38*, 1035–1055. [CrossRef]
22. Alaasar, M. Azobenzene-containing bent-core liquid crystals: An overview. *Liq. Cryst.* **2016**, *43*, 2208–2243. [CrossRef]
23. Niezgoda, I.; Jaworska, J.; Pociecha, D.; Galewski, Z. The kinetics of the E-Z-E isomerisation and liquid-crystalline properties of selected azobenzene derivatives investigated by the prism of the ester group inversion. *Liq. Cryst.* **2015**, *42*, 1148–1158. [CrossRef]
24. Hegde, G.; Shanker, G.; Gan, S.M.; Yuvaraj, A.R.; Mahmood, S.; Mandal, U.K. Synthesis and liquid crystalline behaviour of substituted (E)-phenyl-4-(phenyldiazenyl) benzoate derivatives and their photo switching ability. *Liq. Cryst.* **2016**, *43*, 1578–1588. [CrossRef]
25. Paterson, D.A.; Xiang, J.; Singh, G.; Walker, R.; Agra-Kooijman, D.M.; Martinez-Felipe, A.; Gan, M.; Storey, J.M.D.; Kumar, S.; Lavrentovich, O.D.; et al. Reversible Isothermal Twist-Bend Nematic-Nematic Phase Transition Driven by the Photoisomerization of an Azobenzene-Based Nonsymmetric Liquid Crystal Dinner. *J. Am. Chem. Soc.* **2016**, *138*, 5283–5289. [CrossRef]
26. Al-Zahrani, S.A.; Khan, M.T.; Jevtovic, V.; Masood, N.; Jeilani, Y.A.; Ahmed, H.A.; Alfaidi, F.M. Liquid Crystalline Mixtures with Induced Polymorphic Smectic Phases Targeted for Energy Investigations. *Crystals* **2023**, *13*, 645. [CrossRef]
27. Henderson, P.A.; Cook, A.G.; Imrie, C.T. Oligomeric liquid crystals: From monomers to trimers. *Liq. Cryst.* **2004**, *31*, 1427–1434. [CrossRef]
28. Aldahri, T.H.; Alaasar, M.; Ahmed, H.A. The influence of core fluorination on the phase behaviour of rod-like mesogens. *Liquid Cryst.* **2023**, 1–10. [CrossRef]
29. Srinivasa, H.T. New symmetric azobenzene molecules of varied central cores: Synthesis and characterisation for liquid crystalline properties. *Liq. Cryst.* **2017**, *44*, 1384–1393. [CrossRef]
30. El-Atawy, M.A.; Omar, A.Z.; Alazmi, M.L.; Alsubaie, M.S.; Hamed, E.A.; Ahmed, H.A. Synthesis and characterization of new imine liquid crystals based on terminal perfluoroalkyl group. *Heliyon* **2023**, *9*, e14871. [CrossRef]
31. Wang, M.; Guo, L.X.; Lin, B.P.; Zhang, X.Q.; Sun, Y.; Yang, H. Photo-responsive polysiloxane-based azobenzene liquid crystalline polymers prepared by thiol-ene click chemistry. *Liq. Cryst.* **2016**, *43*, 1626–1635. [CrossRef]
32. Goodby, J.W.; Mandle, R.J.; Davis, E.J.; Zhong, T.; Cowling, S.J. What makes a liquid crystal? The effect of free volume on soft matter. *Liq. Cryst.* **2015**, *42*, 593–622. [CrossRef]
33. Karim, M.R.; Sheikh, M.R.K.; Yahya, R.; Mohamad Salleh, N.; Lo, K.M.; Mahmud, H.E. The effect of terminal substituents on crystal structure, mesophase behaviour and optical property of azo-ester linked materials. *Liq. Cryst.* **2016**, *43*, 1862–1874. [CrossRef]
34. Thaker, B.T.; Kanojiya, J.B.; Tandel, R.S. Effects of different terminal substituents on the mesomorphic behavior of some azo-schiff base and azo-ester-based liquid crystals. *Mol. Cryst. Liq. Cryst.* **2010**, *528*, 120–137. [CrossRef]
35. Naoum, M.M.; Fahmi, A.A.; Alaasar, M.A.; Ahmed, N.H.S. Effect of exchange of terminal substituents on the mesophase behavior of laterally methyl substituted phenylazo benzoates in pure and mixed systems. *Thermochim. Acta* **2011**, *525*, 78–86. [CrossRef]
36. Naoum, M.M.; Ahmed, H.A.; Fahmi, A.A. Liquid crystalline behavior of model compounds di-laterally substituted with different polar groups. *Liq. Cryst.* **2011**, *38*, 511–5199. [CrossRef]
37. Thaker, B.T.; Dhimmar, Y.T.; Patel, B.S.; Solanki, D.B.; Patel, N.B.; Chothani, N.J.; Kanojiya, J. Studies of calamitic liquid crystalline compounds involving ester-azo central linkages with a biphenyl moiety. *Mol. Cryt. Liq. Cryst.* **2011**, *548*, 172–191. [CrossRef]
38. Dixit, S.; Vora, R.A. Novel azoester compounds with a lateral methyl substituent. *Mol. Cryst. Liq. Cryst.* **2014**, *592*, 133–140. [CrossRef]
39. Ahmed, H.A.; Saad, G.R. Mesophase behaviour of laterally di-fluoro-substituted four-ring compounds. *Liq. Cryst.* **2015**, *42*, 1765–1772. [CrossRef]
40. Naoum, M.M.; Metwally, N.H.; Abd Eltawab, M.M.; Ahmed, H.A. Polarity and steric effect of the lateral substituent on the mesophase behaviour of some newly prepared liquid crystals. *Liq. Cryst.* **2015**, *42*, 1351–1369. [CrossRef]

41. Naoum, M.M.; Fahmi, A.A.; Ahmed, N.H.; Saad, G.R. The effect of inversion of the ester group on the mesophase behavior of some azo/ester compounds. *Liq. Cryst.* **2015**, *42*, 1298–1308. [CrossRef]
42. Naoum, M.M.; Fahmi, A.A.; Ahmed, N.H.; Saad, G.R. The effect of lateral methyl substitution on the mesophase behavior of aryl 4-alkoxyphenylazo benzoates. *Liq. Cryst.* **2015**, *42*, 1627–1637.
43. Naoum, M.M.; Fahmi, A.A.; Saad, G.R.; Ali, M.H. Polarity and steric effect of di-lateral substitution on the mesophase behaviour of some azo/ester compounds. *Liq. Cryst.* **2017**, *44*, 1664–1677. [CrossRef]
44. Matsuyama, A.; Kato, T. Phase diagrams of polymer dispersed liquid crystals. *J. Chem. Phys.* **1998**, *108*, 2067–2072. [CrossRef]
45. Naoum, M.M.; Fahmi, A.A.; Abaza, A.H.; Saad, G.R. Effect of exchange of terminal substituents on the mesophase behaviour of some azo/ester compounds. *Liq. Cryst.* **2014**, *41*, 1559–1568. [CrossRef]
46. Cohen, E.; Malka, D.; Shemer, A.; Shahmoon, A.; Zalevsky, Z.; London, M. Neural networks within multi-core optic fibers. *Sci. Rep.* **2016**, *6*, 29080. [CrossRef] [PubMed]
47. Pugachov, Y.; Gulitski, M.; Mizrahi, O.; Malka, D. Design of All-Optical Logic Half-Adder Based on Photonic Crystal Multi-Ring Resonator. *Symmetry* **2023**, *15*, 1063. [CrossRef]
48. Marinescu, D.C.; Pincu, E.; Meltzer, V. Thermal analysis of binary liquid crystals eutectic system cholesteril p-phenoxi phenyl carbamate–cholesteril p-biphenyl carbamate. *J. Therm. Anal. Calorim.* **2012**, *110*, 985–990. [CrossRef]
49. Lu, Z.; Henderson, P.A.; Paterson, B.J.A.; Imrie, C.T. Liquid crystal dimers and the twist-bend nematic phase. The preparation and characterisation of the alpha,omega-bis(4-cyanobiphenyl-4′-yl) alkanedioates. *Liq. Cryst.* **2014**, *41*, 471–483. [CrossRef]
50. Ahmed, H.A. Thermal behavior of binary mixtures of isomers of different molecular structures and different lateral substituent positions. *J. Therm Anal. Calorim.* **2016**, *125*, 823–830. [CrossRef]
51. Abberley, J.P.; Jansze, S.M.; Walker, R.; Paterson, D.A.; Henderson, P.A.; Marcelis, A.T.M.; Storey, J.M.D.; Imrie, C.T. Structure-property relationships in twist-bend nematogens: The influence of terminal groups. *Liq. Cryst.* **2017**, *44*, 68–83. [CrossRef]
52. Alamro, F.S.; Ahmed, H.A.; El-Atawy, M.A.; Al-Zahrani, S.A.; Omar, A.Z. Induced Nematic Phase of New Synthesized Laterally Fluorinated Azo/Ester Derivatives. *Molecules* **2021**, *26*, 4546. [CrossRef]
53. Nafee, S.S.; Hagar, M.; Ahmed, H.A.; El-Shishtawy, R.M.; Raffah, B.M. The synthesis of new thermal stable schiff base/ester liquid crystals: A computational, mesomorphic, and optical study. *Molecules* **2019**, *24*, 3032. [CrossRef]
54. Gomha, S.M.; Ahmed, H.A.; Shaban, M.; Abolibda, T.Z.; Khushaim, M.S.; Alharbi, K.A. Synthesis, optical characterizations and solar energy applications of new Schiff base materials. *Materials* **2021**, *14*, 3718. [CrossRef]
55. Naoum, M.M.; Saad, G.R.; Nessim, R.I.; Abdel-Aziz, T.A.; Seliger, H. Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures II. 4-hexadecyloxyphenyl acrylates and aryl 4-hexadecyloxy benzoates. *Liq. Cryst.* **1997**, *23*, 789–795. [CrossRef]
56. Omar, A.Z.; Alazmi, M.L.; Alsubaie, M.S.; Hamed, E.A.; Ahmed, H.A.; El-Atawy, M.A. Synthesis of New Liquid-Crystalline Compounds Based on Terminal Benzyloxy Group: Characterization, DFT and Mesomorphic Properties. *Molecules* **2023**, *28*, 3804. [CrossRef] [PubMed]
57. Park, J.W.; Bak, C.S.; Labes, M.M. Effects of molecular complexing on the properties of binary nematic liquid crystal mixtures. *J. Am. Chem. Soc.* **1975**, *97*, 4398–4400. [CrossRef]
58. Araya, K.; Matsunaga, Y. Liquid Crystal Formation in Binary Systems. I. An Interpretation of the Phase Diagrams of the Azoxydianisole–Schiff Base Systems. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 989–993. [CrossRef]
59. Dave, J.S.; Lohar, J.M. Liquid-crystalline characteristics of ester mesogens-para-chlorophenyl para′-normal-alkoxycinnamates. *J. Indian Chem. Soc.* **1989**, *66*, 25–27.
60. Lohar, J.M.; Dave, J.S., Jr. Emergence of smectic mesophase in binary mixtures of pure nematogens. *Mol. Cryst. Liq. Cryst.* **1983**, *103*, 181–192. [CrossRef]
61. Mlodziejowski, A. Dissoziation der flüssigen Kristalle. *Z. Phys. Chem.* **1928**, *135*, 129–146. [CrossRef]
62. Gaubert, P. Nouvelle contribution à l'étude des sphérolites (polymorphisme de la codéine, de la thébaïne et de la narcotine). *Bull. Minéral.* **1913**, *36*, 45–64. [CrossRef]
63. Kravchenko, V.M.; Pastukhova, I.S. Dvukhkomponentnye tverdye rastvory i evtekticheskie sistemy indena, izokhinolina, naftalina i benzola. *Zhurnal Prikl. Khimii* **1952**, *25*, 313–321.
64. Dave, J.S.; Menon, M.R.; Patel, P.R. Synthesis and mesomorphic characteristics of mesogens with branched isoamyloxy and isobutyloxy terminal groups. *Mol. Cryst. Liq. Cryst.* **2002**, *378*, 1–11. [CrossRef]
65. Schroeder, J.P.; Bristol, D.W. Liquid crystals. IV. Effects of terminal substituents on the nematic mesomorphism of p-phenylene dibenzoates. *J. Org. Chem.* **1973**, *38*, 3160–3164. [CrossRef]
66. Park, J.W.; Labes, M.M. Broadening of the nematic temperature range by a non-mesogenic solute in a nematic liquid crystal. *Mol. Cryst. Liq. Cryst.* **1976**, *34*, 147–152. [CrossRef]
67. Oh, C.S. Induced smectic mesomorphism by incompatible nematogens. *Mol. Cryst. Liq. Cryst.* **1977**, *42*, 1–14. [CrossRef]
68. Saad, G.R.; Nessim, R.I. Effect of molecular structure on the phase behaviour o some liquid crystalline compounds and their binary mixtures VI [1]. The effect of molecular length. *Liq. Cryst.* **1999**, *26*, 629–636. [CrossRef]
69. Ahmed, H.A.; Mansour, E.; Hagar, M. Mesomorphic study and DFT simulation of calamitic Schiff base liquid crystals with electronically different terminal groups and their binary mixtures. *Liq. Cryst.* **2020**, *47*, 2292–2304. [CrossRef]
70. Alnoman, R.B.; Hagar, M.; Ahmed, H.A.; Naoum, M.M.; Sobaih, H.A.; Almshaly, J.S.; Haddad, M.M.; Alhaisoni, R.A.; Alsobhi, T.A. Binary liquid crystal mixtures based on schiff base derivatives with oriented lateral substituents. *Crystals* **2020**, *10*, 319. [CrossRef]

71. Alhaddad, O.A.; Ahmed, H.A.; Hagar, M.; Saad, G.R.; Abu Al-Ola, K.A.; Naoum, M.M. Thermal and photophysical studies of binary mixtures of liquid crystal with different geometrical mesogens. *Crystals* **2020**, *10*, 223. [CrossRef]
72. Alamro, F.S.; Ahmed, H.A.; Bedowr, N.S.; Naoum, M.M.; Mostafa, A.M.; Al-Kadhi, N.S. New liquid crystals based on terminal fatty chains and polymorphic phase formation from their mixtures. *Crystals* **2022**, *12*, 350. [CrossRef]