Polarity and steric effect of the lateral substituent on the mesophase behaviour of some newly prepared liquid crystals

Magdi M. Naoum*, Nadia H. Metwally, Manal M. Abd eltawab and Hoda A. Ahmed

Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt

(Received 5 January 2015; accepted 6 May 2015)

Eight homologous series of 2- (or 3-) substituted phenyl 4′-(4ʺ-alkoxy phenylazo) benzoates (Iα–h) were prepared in which, within each homologous series, the length of the terminal alkoxy group varies between 6, 8, 10 and 12 carbons, while the other substituent, X, is a laterally attached polar group that alternatively changed from CH₃, H, F, Br and CN. Compounds prepared were characterised by infrared and ¹H-NMR spectroscopy, and their mesophase behaviour investigated by differential scanning calorimetry and identified by polarised light microscopy. The results were discussed in terms of polarity and steric effects. The stability of the mesophase was correlated once with the dipolar anisotropy of the whole molecule and another with the dipolar anisotropy of the substituent, X. A comparative study was made between the investigated compounds and their previously prepared linear 4-substituted isomers, namely 4-substituted phenyl 4′-(4ʺ-alkoxy phenylazo) benzoates (Iα–k).

Keywords: 2- (or 3-) substituted phenyl 4′-(4ʺ-alkoxy phenylazo) benzoates; mesophase behaviour; dipole moment; dipolar anisotropy

1. Introduction

It is well established that the stability of a mesophase in a liquid crystalline compound depends primarily on the anisotropy of intermolecular forces. As a result of lateral attractions, rod-shaped molecules tend to adopt a parallel alignment. Thus, the stability of a mesophase should be greater, the greater the lateral adhesion of linear molecules which in turn would be augmented by an increase of the polarity and/or polarisability of the mesogenic portion of the molecule. In this respect, terminal substituents would affect the polarisability of the aromatic ring to which they are attached. This is attributed [1,2] to increased intermolecular attractions with increasing polarity and polarisability of the mesogenic group. Many series of dimeric liquid crystals have been reported [3–8]; all of these compounds may be termed symmetric, with identical mesogenic moieties, or non-symmetric dimers, with different mesogenic units. In both the cases, the specific interactions between the two mesogenic groups do lead to a significant variation in the mesophase behaviour of such materials.

Generally, lateral substitution increases the breadth of the laterally unsubstituted molecule and, as a result, the long narrow molecules are forced apart, reducing the strength of intermolecular attraction.[9] However, the replacement of a lateral hydrogen atom by a polar atom or group produces an additional dipole moment into the molecule. Thus, the introduction of a substituent into a side position of a mesomorphic molecule would have two opposing effects: (a) a decrease in the mesomorphic thermal stability due to increased separation of the long axes of the molecules [10] and (b) an increase in its polar anisotropy due to its polarising effect. Furthermore, the positions of the lateral substituents are important since they affect, to differing extents, the conjugation with the ring they are attached to. In addition, different positions of the lateral substituent result in the protrusion of the side group with different angles. Finally, the influence of the size of the substituent is also pronounced.[11–20]

Generally, linking units containing multiple bonds, e.g. –N=N– or –CH=N– groups, that maintain the rigidity and linearity of the molecules are satisfactory in promoting mesophase stability. However, ester linkage contains no multiple bonds in the chain of atoms linking the two benzene rings, and conjugative interactions within the ester moiety and the rings do lead to some double bond character; hence, the mesophase becomes more persistent when the phase stability effect of the mutual conjugation between the substituent and the ester carbonyl or oxygen is increased. On the other hand, azo-based liquid crystals have attracted considerable attention because of their potential application in optical storage.[21] Therefore, the azo-ester mesogens were chosen because of their remarkable thermal stability; in addition, they are attractive with regard to their photo-induced effect.[21–27]
The present work aims to prepare some three-ring azo/ester compounds, \( \text{In}_{a,h} \), possessing two unsymmetrical wing groups. The first wing, attached to the phenyl azo moiety, is an alloky group with chain length that varies between 6 and 12 carbons. The second wing group, attached to the phenyl benzoate moiety, is a lateral polar substituent that changes between the electron-donating (\( \text{CH}_3 \)) and electron-withdrawing (\( \text{F}, \text{Br} \) and \( \text{CN} \)) substituents, including the terminally unsubstituted analogues. Polar substituents are attached to positions 2- or 3- of one of the terminal rings. Lateral substituents, introduced into different positions of the terminal ring of compounds, are chosen to be of variable size (e.g. \( \text{F} \) and \( \text{Br} \)) and different orientation aiming to investigate their steric and polarisability effects that influence the lateral association and, consequently, the stability of the solid and mesophases. The effect of polarity, position and orientation of the lateral substituents, as well as the length of the alkoxy chain, on the mesophase behaviour of the prepared compounds (\( \text{In}_{a,h} \)) will be investigated and compared with their previously investigated linear isomers, \( \text{In}_{i-k} \), substituted in position-4.

2. Experimental

Chemicals used were of very pure grades and purchased from the following companies: Fluka, Buchs, Switzerland; MP Biomedicals, Inc., Illkirch, France; BDH, Poole, England; Aldrich, Wisconsin, USA; and E. Merck, Darmstadt, Germany.

2.1. Physical characterisation

Infrared absorption spectra were measured with a Perkin-Elmer B25 spectrophotometer, and \( ^1\text{H}-\text{NMR} \) spectra with a Varian EM 350L. Calorimetric measurements were carried out using a differential scanning calorimeter, PL-DSC, of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammena, et al. [22] DSC measurements were carried out for small samples (2–3 mg) placed in sealed aluminium pans. All measurements were achieved at a heating rate of 10°C/min in inert atmosphere of nitrogen gas (10 ml/min).

Transition temperatures were checked and type of mesophase identified for all compounds prepared with a standard polarised light microscope (PLM) (Wild, Germany) attached to a homemade hot-stage.

The purity of samples prepared was checked with thin-layer chromatography using TLC sheets coated with silica gel (E. Merck), whereby spots were detected by a UV-lamp.

2.2. Preparation of materials

The new azo/esters (\( \text{In}_{a,h} \)) were prepared according to Scheme 1.

\[
C_nH_{2n+1}O-\begin{array}{c}
\text{N=N} \\
\text{COO-}
\end{array}X
\]

(\( \text{In}_{a,b} \))

a, \( X = 2-\text{CH}_3; \) b, \( X = 3-\text{CH}_3; \) c, \( X = \text{H}; \) d, \( X = 2-\text{F}; \) e, \( 2-X = 3-\text{F}; \)

f, \( X = 2-\text{Br}; \) g, \( X = 3-\text{Br}; \) and h, \( X = 3-\text{CN} \)

\[
C_nH_{2n+1}O-\begin{array}{c}
\text{N=N} \\
\text{COO-}
\end{array}X
\]

(\( \text{In}_{i-k} \))

i, \( X = \text{CH}_3; \) j, \( X = \text{Br}; \) and k, \( X = \text{CN} \)

2.2.1. Preparation of ethyl-4-hydroxyphenylazo benzoate (\( \text{A} \))

Ethyl-4-amino benzoate (0.01 mol) was dissolved in concentrated hydrochloric acid (HCl) and cooled in ice-salt bath to 0°C. To the resulting solution, a cold aqueous solution of sodium nitrite (0.03 mol) was added drop-wise with stirring. During the addition, the temperature did not exceed 2°C. After complete addition, the cold mixture was added drop-wise to an ice-cold solution of phenol (0.01 mol) in sodium hydroxide (0.03 mol). The mixture was further stirred at 0°C for 1 h and then acidified with dilute HCl. The solid separated was
filtered and crystallised twice from ethanol. The product was TLC pure and gave melting point 163°C that agreed with that reported in the literature.[23]

2.2.2. Preparation of ethyl 4-n-alkoxy phenylazo benzoates (Bn)
These were prepared by the method described previously.[24] Ethyl-4-hydroxyphenylazo benzoate (0.001 mol) in alcoholic KOH (0.02 mol) to which the appropriate amount of 1-bromo-n-alkane (0.0012 mol) was added drop-wise while stirring. Stirring was continued at room temperature for 2 days. The solid separated was filtered off, the solution evaporated and the residue crystallised twice from ethanol. The products were TLC pure and give transition temperatures as given in the literature.[24]

2.2.3. Preparation of 4-n-alkoxy phenylazo benzoic acids (An)
The esters (Bn) were hydrolysed to the corresponding acids by refluxing in aqueous ethanolic potassium hydroxide for 24 h and then acidified by dilute HCl to give the corresponding acids. Again the products were crystallised twice from ethanol to give TLC pure solids that give transition temperatures that agree with those reported in the literature.[25]

2.2.4. Preparation of 2- (or 3-) substituted phenyl-4-n-alkoxy phenylazo benzoates (Ina-h)
Molar equivalents of 4-n-alkoxy phenylazo benzoic acid (An) and 2- (or 3-) substituted phenol (0.001 mol each) were dissolved in 25 ml of dry methylene chloride. To the resulting mixture, dicyclohexylcarbodiimide (0.002 mol) and few crystals of 4-(dimethylamino) pyridine, as a catalyst, were added and the mixture stirred at room temperature for 3 days. The solvent was distilled off and the residue crystallised twice from ethanol. The products obtained were TLC pure and gave transition temperatures as given in Table 1.

2.3. Confirmation of molecular structure
The molecular formulae of the newly prepared derivatives (Ina-h) were confirmed by elemental analysis, ¹H-NMR and mass spectroscopy. The results were in agreement with the expected structures within acceptable limits. As an example, infrared spectra and ¹H-NMR spectra of series Ina-h are summarised in Tables 2 and 3, respectively.

3. Results and discussion
¹H-NMR data showed the expected integrated aliphatic to aromatic proton ratios in all the compounds investigated. Since almost identical infrared absorption spectra were observed for all the members of the eight homologous series (Ina-h), the absorption bands of compounds in series Ina-h, with their assignments, are given as representative examples in Table 2. Corresponding absorption bands [21] for the 4-substituted isomers, Ina-h, are given before.[21]

Investigation of the infrared absorption bands of the ester carbonyl group revealed that neither the
### Table 1. Transition temperatures (°C) and (transition enthalpy in kJ/mol) of the azo/esters, \( I_{nt-h} \).

| Compound no. | \( n \) | \( X \) | \( T_{C-A} \) | \( T_{C-N} \) | \( T_{A-N} \) | \( T_{A-I} \) | \( T_{N-I} \) |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| \( I_{6a} \) | 6      | 2-CH\(_3\) | –      | 117 (91.8) | –      | –      | 139 (4.1) |
| \( I_{6b} \) | 3      | 3-CH\(_3\) | 92 (89.5) | –      | 110 (2.96) | –      | 162 (1.44) |
| \( I_{6c} \) | H      | 110 (85.6) | –      | 127 (8.3) | –      | 165 (6.4) |
| \( I_{6d} \) | 2-F    | 90 (52.7) | –      | 110 (1.55) | –      | 146 (5.32) |
| \( I_{6e} \) | 3-F    | 108 (43.8) | –      | 117 (0.9) | –      | 154 (8.3) |
| \( I_{6f} \) | 2-Br   | –      | 103 (44.7) | –      | –      | 125 (3.6) |
| \( I_{6g} \) | 3-Br   | –      | 121 (96.5) | –      | –      | 159 (3.8) |
| \( I_{6h} \) | 3-CN   | –      | 110 (27.1) | –      | –      | 187 (4.3) |
| \( I_{8a} \) | 8      | 2-CH\(_3\) | 112 (90.7) | –      | –      | 135 (2.1) |
| \( I_{8b} \) | 3-CH\(_3\) | 98 (76.6) | –      | 117 (1.11) | –      | 155 (3.53) |
| \( I_{8c} \) | H      | 120 (34.4) | –      | 139 (1.5) | –      | 153 (1.1) |
| \( I_{8d} \) | 2-F    | 100 (28.7) | –      | 116 (1.21) | –      | 128 (0.48) |
| \( I_{8e} \) | 3-F    | 104 (20.3) | –      | 124 (1.9) | –      | 136 (4.95) |
| \( I_{8f} \) | 2-Br   | –      | 110 (43.8) | –      | –      | 115 (0.91) |
| \( I_{8g} \) | 3-Br   | –      | 118 (98.4) | –      | –      | 146 (1.72) |
| \( I_{8h} \) | 3-CN   | 107 (33.9) | –      | 120 (0.81) | –      | 138 (0.63) |
| \( I_{8i} \) | 4-CH\(_3\) | 109 (24.5) | –      | 134 (1.9) | –      | 230 (1.3) |
| \( I_{8j} \) | 4-Br   | –      | 136 (24.2) | –      | –      | 213 (1.3) |
| \( I_{8k} \) | 4-CN   | –      | 131 (39.0) | –      | –      | 251 (0.64) |
| \( I_{10a} \) | 10     | 2-CH\(_3\) | 118 (103.5) | –      | –      | 134 (3.5) |
| \( I_{10b} \) | 3-CH\(_3\) | 87 (32.8) | –      | 124 (0.51) | –      | 138 (0.52) |
| \( I_{10c} \) | H      | 95 (32.4) | –      | –      | 145 (1.9) | –      |
| \( I_{10d} \) | 2-F    | 99 (26.9) | –      | 119 (0.97) | –      |
| \( I_{10e} \) | 3-F    | 105 (36.6) | –      | 126 (2.3) | –      |
| \( I_{10f} \) | 2-Br   | –      | 105 (135.8) | –      | –      |
| \( I_{10g} \) | 3-Br   | –      | 97 (31.2) | –      | –      |
| \( I_{10h} \) | 3-CN   | 97 (37.9) | –      | –      | 118 (0.97) |
| \( I_{10i} \) | 4-CH\(_3\) | 101 (28.0) | –      | 172 (3.6) | –      |
| \( I_{10j} \) | 4-Br   | 101 (53.5) | –      | –      | 146 (4.2) |
| \( I_{10k} \) | 4-CN   | 91 (56.5) | –      | –      | 148 (2.9) |
| \( I_{12a} \) | 12     | 2-CH\(_3\) | 109 (85.6) | –      | –      | 132 (2.6) |
| \( I_{12b} \) | 3-CH\(_3\) | 100 (64.2) | –      | –      | 114 (2.68) |
| \( I_{12c} \) | H      | 127 (27.3) | –      | –      | 143 (1.4) |
| \( I_{12d} \) | 2-F    | 97 (49.6) | –      | –      | 117.5(6.5) |
| \( I_{12e} \) | 3-F    | 110 (22.1) | –      | –      | 128 (6.5) |
| \( I_{12f} \) | 2-Br   | –      | 94 (133.9) | –      | –      |
| \( I_{12g} \) | 3-Br   | –      | 94 (39.7) | –      | –      |
| \( I_{12h} \) | 3-CN   | 106 (50.5) | –      | 102 (1.2) |
| \( I_{12i} \) | 4-CN   | 90 (20.5) | –      | 176 (1.3) | –      |
| \( I_{12j} \) | 4-Br   | 121 (49.9) | –      | 146 (2.1) |
| \( I_{12k} \) | 4-CN   | 106 (55.4) | –      | 160 (1.4) |

Notes: Cr–A denotes transition from solid to the SmA phase. Cr–N denotes transition from solid to the N phase. A–N denotes transition from SmA to the N phase. A–I denotes transition from SmA to the isotropic phase. N–I denotes transition from nematic to the isotropic phase.

### Table 2. Infrared absorption spectra of compounds I/2\(_{a-e}\).

| Compound no. | \( X \) | \( v_{C=O} \) | \( v_{C=O} \) | \( v_{C=O} \) | \( v_{C=O} \) | \( N_{C=O} \) | \( N_{C=O} \) |
|--------------|--------|--------|--------|--------|--------|--------|--------|
| \( I_{2a} \) | 2-CH\(_3\) | 2921 | 2851 | 1733 | 1598 | 1469 | 1252 |
| \( I_{2b} \) | 3-CH\(_3\) | 2923 | 2851 | 1732 | 1586 | 1468 | 1241 |
| \( I_{2c} \) | H      | 2920 | 2851 | 1734 | 1598 | 1492 | 1259 |
| \( I_{2d} \) | 2-F    | 2922 | 2851 | 1745 | 1602 | 1499 | 1253 |
| \( I_{2e} \) | 3-F    | 2925 | 2851 | 1735 | 1577 | 1491 | 1250 |
| \( I_{8a} \) | 2-Br   | 2921 | 2580 | 1738 | 1594 | 1495 | 1254 |
| \( I_{8b} \) | 3-Br   | 2925 | 2851 | 1730 | 1577 | 1465 | 1248 |
| \( I_{8c} \) | 3-CN   | 2919 | 2851 | 1736 | 1595 | 1497 | 1255 |
| \( I_{8d} \) | 4-CH\(_3\) | 2919 | 2851 | 1734 | 1601 | 1505 | 1251 |
| \( I_{8e} \) | 4-Br   | 2920 | 2851 | 1733 | 1599 | 1487 | 1258 |
| \( I_{8f} \) | 4-CN   | 2923 | 2854 | 1732 | 1601 | 1501 | 1258 |
length of the alkoxy group, \( n = 6 - 12 \), in any of the homologous series, \( \text{I}_{n} \), nor the lateral substituent, in any group of derivatives bearing the same alkoxy group, e.g. \( \text{I}_{2a-h} \), had a significant effect on the absorption associated with the carbonyl group (1732–1745 cm\(^{-1}\)). These findings are in agreement with the absorption previously recorded for the laterally 2-methyl and 2-chloro-substituted \([26] \) isomers, \( \text{II} \).

3.1. Mesophase behaviour of the investigated compounds

Since, as mentioned above, the mesophase stability of a mesomorphic compound depends mainly upon intermolecular attractions in which molecular polarity plays a significant role, it has been shown \([28] \) that within one series of compounds the dipole moment of an individual compound is determined by the nature of the substituents. A change in the extent of conjugation alters the polarisability and resultant dipole moment of the molecule. It has also been shown \([29] \) that the dipole moments of all members of a homologous series are virtually the same, irrespective of the alkoxy-chain length. This result is supported by the fact that alkoxy groups have similar polarity regardless of their length, and at the same time they do not affect the degree of conjugative interaction between the alkoxy oxygen and the ester carbonyl, as is confirmed by infrared measurements.

Transition temperatures and enthalpies measured by DSC, and the phases identified by PLM, for the newly prepared compounds \( \text{I}_{n} \), are summarised in Table 1; corresponding data for 4-substituted compounds \( \text{I}_{n} \) are given elsewhere.\([21] \) The effect of increasing alkoxy-chain length on the mesophase behaviour of compounds in series \( \text{I}_{n} \), is depicted graphically in Figure 1 and those of their isomers \( \text{I}_{n} \), for comparison, are depicted with their corresponding 2- (and 3-) substituted isomers in Figure 2. It will be seen from Table 1 and Figures 1 and 2 that, when comparison is made between the three differently substituted positional isomers (i.e. in positions

Table 3. \(^{1}\)H-NMR spectra and their assignments for compounds \( \text{I}_{a-e} \).

| Compound no. | X   | 1 (t, 2 H) | 2 (m,18 H) | 3 (q, 2 H) | 4 (t, 2 H) | 5 (d, 2 H) | 6 (d, 2 H) | 7 (d, 2 H) | 8 (d, 2 H) | 9 (d, 2 H) | 10 (d, H) |
|--------------|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| \( \text{I}_{2a} \) | 2-CH\(_3\) | 0.91 | 1.32 | 1.72 | 3.98 | 7.01 | 7.82 | 8.02 | 8.07 | 6.61 | 6.90 |
| \( \text{I}_{2b} \) | 3-CH\(_3\) | 0.91 | 1.30 | 1.72 | 3.99 | 7.01 | 7.85 | 8.03 | 8.07 | 6.54 | 6.97 |
| \( \text{I}_{2c} \) | H   | 0.91 | 1.31 | 1.72 | 4.12 | 7.01 | 7.82 | 8.02 | 8.07 | 6.98 | 7.09 |
| \( \text{I}_{2d} \) | 2-F  | 0.91 | 1.30 | 1.72 | 3.99 | 7.01 | 7.82 | 8.03 | 8.07 | 6.71 | 6.85 |
| \( \text{I}_{2e} \) | 3-F  | 0.86 | 1.32 | 1.73 | 4.10 | 7.15 | 7.93 | 7.94 | 8.13 | 6.50 | 7.07 |
| \( \text{I}_{2f} \) | 2-Br | 0.91 | 1.30 | 1.72 | 3.97 | 7.01 | 7.82 | 8.02 | 8.07 | 6.59 | 7.01 |
| \( \text{I}_{2g} \) | 3-Br | 0.86 | 1.32 | 1.71 | 4.09 | 7.13 | 7.91 | 7.94 | 8.13 | 6.67 | 6.98 |
| \( \text{I}_{2h} \) | 3-CN | 0.91 | 1.30 | 1.72 | 3.99 | 7.01 | 7.82 | 8.02 | 8.07 | 7.01 | 7.27 |

It is clear that the introduction of the weakly electron-donating methyl substituent adjacent to the oxygen of the ester group on the central benzene ring \([26] \) slightly affected the polarisability of the ester carbonyl group in series \( \text{II} \), with C=O absorption at a slightly lower frequency. Alternatively, the electron-withdrawing character of the chlorine atom in the same position of the central ring \([27] \) was accompanied by a slight increase in the double bond character of the ester carbonyl, and absorption was consequently at a slightly higher frequency. These findings suggested that the effect of either type of substituents (CH\(_3\) or Cl), adjacent to the ester oxygen atom, on the polarity of the final product was relatively slight. The same was found true in the present series of compounds, \( \text{I} \), where the electron-donating substituent, CH\(_3\), or the electron-withdrawing, F, Br, CN, groups in either the 2- or 3- positions of the terminal ring, again adjacent to the ester oxygen atom, proved to have but little effect on the absorption of the ester carbonyls.
2-, 3- and 4-, Figure 2), the stability and type of the mesophase produced are dependent on two factors. First is the enhanced dipole of the mesogenic portion of the molecule which is remarkably dependent on the position to which the polar group is introduced. The second factor is a steric one which again varies according to the size and position of the substituent. In the investigated group of isomers, upon para substitution (in position-4), the electron-withdrawing substituent (Br or CN) is accompanied with an increase in the dipole moment, as will be seen later, with no steric effect (Scheme 2). Such enhanced dipole is expected to induce high stability to the mesophase.

Conversely, the electron-donating weak polar (CH₃) substituent, also in position-4, having again no steric effect is expected to have a dipole moment close to the unsubstituted one (X=H) and consequently a mesophase stability very close too (Scheme 3).

On the other hand, when substitution is made in the lateral 2- or 3-positions, which make, respectively, an angle of 60° and 120° with the major longitudinal axis of the molecule, the dipole moment will be differently affected according to the position and polarity of the group. Thus, in the case of the electron-withdrawing substituents (F or Br) the resultant dipole moment will be lower (when in position-2) and greater (when in position-3) upon substitution (Schemes 4 and 5).

Figure 1. Effect of alkoxy-chain length \(n\) on transition temperatures \(°C\) of compounds (a) \(\text{In}_a-\text{In}_d\) and (b) \(\text{In}_e-\text{In}_h\).
In case of the electron-donating (CH$_3$) group, the reverse holds good but with very small differences in the dipole moments. Such variation in the polarity is expected to be accompanied by a parallel behaviour in the stability of the mesophase (Schemes 6 and 7).

3.2. Mesophase stability and conformational structure of the molecule

Generally, the mesophase behaviour of a calamitic mesogen is a direct effect of molecular–molecular interactions as well as the stereo electronic properties of the molecule. In the present group of compounds (I$_{k_a,b}$), molecular association of the rod-like molecules, and consequently their mesophases stability ($T_c$), depends on several interfering factors, namely

1. Lateral adhesion of linear molecules that increases with the increase of the alkoxy-chain length ($n$).
2. End-to-end interaction that differs according to the size, position and polarity of the substituent leading to variable steric effects.
3. The steric effects of substituent may lead to variable conformations as a result of the enforced rotation around the X-phenyl-O-bond; thus, the following two planar conformations are equally possible:
Figure 2. Comparison of clearing temperatures ($T_c$) of various positional isomers with unsubstituted ones.

Scheme 2. Polarisation in electron-withdrawing 4-CN-substituted homologue.

Scheme 3. Polarisation in the 4-CH$_3$-substituted homologues.
It should be mentioned here that only planar conformations are possible since all the investigated derivatives (I_{n-k}) are mesomorphic, while a non-planar conformation definitely destroys any possible mesophases. In this respect, linear substitution, in position-4, will lead to one conformation and, consequently, the stability of the mesophases ($T_C$) was found [21] to correlate with the polarisability anisotropy, $\Delta \alpha_X$, of the 4-substituent, $X$. 

Scheme 4. Polarisation in the electron-withdrawing 2-substituted homologues.

Scheme 5. Polarisation in the electron-withdrawing 3-substituted homologues.

Scheme 6. Polarisations in the 2-CH$_3$-substituted homologues.

Scheme 7. Polarisations in the 3-CH$_3$-substituted homologues.
Investigating the resultant effect of all these three factors on the mesophase stability ($T_C$) of the differently substituted derivatives ($I_n_{x,k}$), $T_C$ values were found to decrease according to $X$ in the following order:

(A) According to the position of the same substituent $X$ and compared to the parent unsubstituted derivative ($X=H$):

(i) $n = 6$
- $H > 3-\text{CH}_3 > 2-\text{CH}_3$
- $H > 3-\text{F} > 2-\text{F}$
- $H > 3-\text{Br} > 2-\text{Br}$
- $3-\text{CN} > H$

(ii) $n = 8$
- $4-\text{CH}_3 > 3-\text{CH}_3 = H > 2-\text{CH}_3$
- $H > 3-\text{F} > 2-\text{F}$
- $4-\text{Br} > H > 3-\text{Br} > 2-\text{Br}$
- $4-\text{CN} > H > 3-\text{CN}$

(iii) $n = 10$
- $4-\text{CH}_3 > H > 3-\text{CH}_3 > 2-\text{CH}_3$
- $H > 3-\text{F} > 2-\text{F}$
- $H > 3-\text{Br} > 4-\text{Br} > 2-\text{Br}$
- $H > 4-\text{CN} > 3-\text{CN}$

(iv) $n = 12$
- $4-\text{CH}_3 > H > 2-\text{CH}_3 > 3-\text{CH}_3$
- $H > 3-\text{F} > 2-\text{F}$
- $3-\text{Br} > H = 2-\text{Br} > 3-\text{Br}$
- $4-\text{CN} > H > 3-\text{CN}$

(B) According to the polarity of substituent occupying the same position:

(i) $n = 6$
- $H > 2-\text{F} > 2-\text{CH}_3 > 2-\text{Br}$
- $3-\text{CN} > H > 3-\text{CH}_3 > 3-\text{Br} > 3-\text{F}$

(ii) $n = 8$
- $H > 2-\text{CH}_3 > 2-\text{F} > 2-\text{Br}$
- $3-\text{CH}_3 > H > 3-\text{Br} > 3-\text{CN} > 3-\text{F}$
- $4-\text{CN} > 4-\text{Br} > H > 4-\text{CH}_3$

(iii) $n = 10$
- $H > 2-\text{CH}_3 > 2-\text{F} > 2-\text{Br}$
- $H > 3-\text{Br} > 3-\text{CH}_3 > 3-\text{F} > 3-\text{CN}$
- $4-\text{CH}_3 > H > 4-\text{CN} > 4-\text{Br}$

(iv) $n = 12$
- $H > 2-\text{CH}_3 > 2-\text{F} > 2-\text{Br}$
- $H > 3-\text{Br} > 3-\text{F} > 3-\text{CH}_3 > 3-\text{CN}$
- $4-\text{CH}_3 > 4-\text{CN} > 4-\text{Br} > H$

In both types of comparison (A and B), missing derivatives are not available. From these two types of comparison, it can be concluded that no one order of decrease in the mesophase stability is applicable for all values of $n$. For instance, in terms of Van der Waals radii, the Br atom is larger than the F atom and, hence, it is more polarisable because the valance electrons residing at this atom are far apart from the nucleus.[30] The presence of a polarisable Br atom at the terminal increases the overall intermolecular attraction.[31] Although the methyl ($\text{CH}_3$) group favours the space filling at the molecular terminal more effectively than the Br atom due to the larger size of the former, for $n > 10$ carbon atoms, the 4-$\text{CH}_3$ substituted homologues showed higher thermal stability than their unsubstituted or Br-substituted analogues.[32] This conclusion indicates that the length of the alkoxy chain has a significant factor that directs both conformation and steric effect.

3.3. Mesophase stability and dipolar anisotropy of the whole molecule

As mentioned above, since all members of the laterally substituted eight homologous series ($I_n_{a,h}$) are mesomorphic, therefore they should all exist in a planar conformation. That is, all the three benzene rings should be co-planar; otherwise, any possible rotation around a single bond by an angle differing from 180° would result in a non-planar conformation and, consequently, in the disruption of the mesomeric conjugation and of the mesophase stability. This will be confirmed via the calculation of the theoretical dipole moments, using Gaussian 5.0 program, of planar conformations as represented in Scheme 8. The results of computations are collected in Table 4. As
Table 4. Calculated dipole moments ($\mu_{\text{calc}}$) of the probable structures for the homologous series, $I_n$, with their longitudinal ($\mu_x$), lateral ($\mu_y$), and dipolar anisotropy, $\Delta \mu$.

| Series X | $\mu_{\text{calc}}$ (D) | $\mu_x$ (D) | $\mu_y$ (D) | $\mu_z$ (D) | $\Delta \mu$ (D) |
|-----------|-----------------|------------|------------|------------|-------------|
| $I_{n_1}$ | 2-CH$_3$        | 3.7954     | -0.8645    | -3.6956    | -0.0192     | 2.83        |
| $I_{n_1}$ | 3-CH$_3$        | 3.4184     | -1.0377    | -3.2570    | -0.0129     | 2.22        |
| $I_{n_1}$ | H               | 3.5068     | 0.6199     | 3.4515     | -0.0192     | 2.84        |
| $I_{n_1}$ | 2-F             | 2.5392     | -0.7085    | 2.4373     | -0.0725     | 3.15        |
| $I_{n_1}$ | 3-F             | 4.8591     | 1.2431     | -4.6960    | -0.1126     | 5.94        |
| $I_{n_1}$ | 2-Br            | 2.8082     | 0.5827     | -2.7465    | -0.0572     | 3.33        |
| $I_{n_1}$ | 3-Br            | 5.3498     | -1.7501    | -5.0553    | 0.0250      | 3.31        |
| $I_{n_1}$ | 3-CN            | 6.9184     | 3.3758     | -6.0365    | -0.1693     | 9.41        |
| $I_{n_1}$ | 4-CH$_3$        | 3.0928     | 0.7381     | 3.0035     | -0.0094     | 2.27        |
| $I_{n_1}$ | 4-Br            | 5.7443     | 0.4149     | 5.7288     | -0.0456     | 5.31        |
| $I_{n_1}$ | 4-CN            | 8.8686     | -0.0163    | 8.8680     | -0.0093     | 8.88        |

can be seen from Table 4, the out-of-plane components of the dipole moments ($\mu_y$) for all derivatives are nearly zero, indicating planar conformations. At this stage, it may be of help to collect the dipole moment components, $\mu_x$ and $\mu_y$, for each homologous series, calculated by the same program in Table 4. It should be mentioned here, as shown in Scheme 8, that $\mu_y$ is the dipole moment component along the longitudinal axis of the molecule, and $\mu_x$ is accordingly the lateral (in-plane perpendicular) component in such a way that $\mu^2 = \mu_y^2 + \mu_x^2$.

Van der Veen [33] has deduced an equation that relates the clearing temperature ($T_c$) to the polarisability anisotropy of the bonds, $C_{A^\alpha-X}$, to small compact substituents. The equation can be put in the form [34]

$$\sqrt{T_c} = a.\Delta \alpha_M + a.\Delta \alpha_x$$  \hspace{1cm} (1)$$

where $\Delta \alpha_x$ is the anisotropy of polarisability of the bond to the linear substituent X, and $\Delta \alpha_M$ is the anisotropy of polarisability of the whole molecular structure except the substituent X. This equation is non-applicable to the present group of compounds since lateral substitutions are used. In order to investigate the effect of dipole moment on the stability of the mesophase exhibited by compounds $I_{n_1}$, values of $\sqrt{T_c}$ are plotted as function of the molecular dipole moments, $\mu$, in Figure 3. As can be seen from Figure 3, the $\sqrt{T_c}$ are irregularly correlated with the total dipole moment of the compound. The weak $\sqrt{T_c}$ dependency on the dipole moment can be attributed to both strong steric interaction of the lateral substituent, as well as to the relatively weak conjugative interaction between the lateral substituent and the mesogenic portion of the molecule, which varies according to its position. In order to decide which component of the dipole moment is more pronounced on the lateral adhesion between neighbouring rod-like molecules that leads to stabilisation of the mesophase, values of $\sqrt{T_c}$ are plotted once as function of the lateral, $\mu_y$, and another against the longitudinal, $\mu_x$, components of the dipole moments in Figures 4 and 5, respectively. Comparison between these two figures revealed that the dependency on the lateral and longitudinal components, $\mu_x$ and $\mu_y$, parallels that with the total dipole moment (see Figures 3–5). This is expected since lateral adhesion is highly affected by the steric effect of lateral substituents compared with the increase of dipole moment. That is, the bulky CH$_3$ substituents, in $I_{n_1}$ and $I_{n_2}$, in spite of their increased $\mu_x$ and $\mu_y$ values with respect to $I_{n_3}$, react sterically to decrease the stability of their mesophases, especially in the lower homologues, $n = 6$. The higher mesophase stability values for the 3-CN homologues are attributed to the high increase in both dipole moment components ($\mu_x$ and $\mu_y$).

Since the anisotropy of molecular structure is generally reflected into a dipolar anisotropy ($\Delta \mu = \mu_x - \mu_y$), it would be worthy to investigate the effect of the latter value ($\Delta \mu$) on the mesophase behaviour of the compounds (Figure 6). Again as can be seen from Figure 6, the mesophase stability parallel that with $\mu_x$. These behaviours revealed that little mesomeric interaction takes place while the steric interaction leads to destabilisation of the mesophase, when comparison is made with the 4-substituted analogues.

These expectations were found to be true; the mesophase stability (clearing temperatures, $T_{A,1}$ or $T_{A,1}$) was found to decrease depending on the polarity and position of the substituent X as:

1. For $n = 6$, para isomers are not available
   - X = CH$_3$; ortho > meta,
   - X = F; meta > ortho,
   - X = Br; meta > ortho
   - X = CN; para > meta.

2. For $n = 8$
   - X = CH$_3$; para > ortho > meta
   - X = F; para > meta = ortho
   - X = Br; para > meta > ortho
   - X = CN; para > meta; ortho isomer is not prepared

3. For $n = 10$
   - X = CH$_3$; para > ortho > meta
   - X = F; meta > ortho; para isomer is not available
   - X = Br; para > meta > ortho
   - X = CN; para > meta; ortho isomer is not prepared

(1) For $n = 6$, para isomers are not available

(2) For $n = 8$

(3) For $n = 10$
Figure 3. Dependence of $\sqrt{T_C}$ on the total dipole moment ($\mu$) for compounds $I_{n-k}$.

Figure 4. Dependence of $\sqrt{T_C}$ on the lateral component of the dipole moment ($\mu_x$) for compounds $I_{n-k}$. 
Figure 5. Dependence of $\sqrt{T_C}$ on the longitudinal component of the dipole moment ($\mu_x$) for compounds Ina–k.

Figure 6. Dependence of $\sqrt{T_C}$ on the dipolar anisotropy ($\Delta \mu$) for compounds Ina–k.
(4) For \( n = 12 \)
- \( X = \text{CH}_3 \); para > ortho > meta
- \( X = \text{F}; \) meta > ortho; para isomer is not available
- \( X = \text{Br}; \) para > meta > ortho
- \( X = \text{CN}; \) para > meta; ortho isomer is not prepared

3.4. Mesophase stability and dipolar anisotropy of the \( C_{A^i}X \) group moment

From Equation (1), one can deduce that the anisotropy of polarisability of the whole molecular structure, \( \Delta \alpha_{SM} \), for a given series of derivatives, except the polar substituent, \( X \), is a constant value independent of the type or position of \( X \). Accordingly, irrespective of the polarity and/or position of the substituent \( X \), the whole molecular structure, except the polar substituent, \( X \), will have a constant value.

Actually, values for the anisotropy of polarisability, \( \Delta \alpha_{x} \), are applicable for substituents in position-4. So, we are going to calculate the two components of group moments substituted in the 2-, 3- and 4-positions; the first \( (\mu_{x}') \) is, as in Scheme 8, in the 1,4-direction of the benzene ring to which \( X \) is substituted, which will be along the longitudinal axis of the molecule, while the second component \( (\mu_{y}') \) will be in the perpendicular direction, taken as positive in the side of the C=O bond. In this respect:

(1) Substituents in position-4 will have no \( \mu_{x}' \) value, whereas \( \mu_{y}' \) is equal to the group moment with a direction dependent on whether it is an electron-donating or electron-withdrawing substituent. Thus, for the derivatives in compounds \( In_{i-k} \), the 4-CH\(_3\) substituent will have group moment \( \mu' = 0.4 \) D directed towards the remainder of the molecule and, consequently, given a negative value. Conversely, the 4-CN group will have group moment \( (3.99 \) D) directed in the reverse direction, thus, possessing a positive value.

(2) Substituents in the meta position, i.e. in position-3, with group moment \( \mu' \), its two components will be calculated as \( \mu_{x}' = \mu' \cos 120^\circ \) and \( \mu_{y}' = \mu' \sin 120^\circ \).

(3) Finally, the two group moment components for substituents in the ortho position, i.e. in position-2, will be given by \( \mu_{x}' = \mu' \cos 60^\circ \) and \( \mu_{x}' = \mu' \sin 60^\circ \).

In such a way the dipolar anisotropy \( \Delta \mu' \) is given by \( \mu_{x}' - \mu_{y}' \).

Values for \( \mu_{x}', \mu_{y}' \) and \( \Delta \mu' \) were calculated for all substituents investigated, and the results are collected in Table 5.

Parallel correlations as those made with the dipole moment of the whole molecular structures are reproduced with the group moment components, \( \mu_{x}', \mu_{y}' \) and \( \Delta \mu' \), in Figures 7–9, respectively. As shown in Figure 7, negative dependence of \( \sqrt{T_C} \) on \( \mu_{x}' \) is observed for the shortest homologues, \( n = 6 \), and changes to a positive ones as \( n \) increases. Also observed in Figure 7, independent of \( n \), the unsubstituted homologues are always above the correlation lines, indicating that lateral substitution is accompanied by destabilisation of the mesophase. The linear substituents, in position-4, have no moment components in the \( x \)-axis, so they do not appear in this correlation. With respect to the longitudinal components of the bond moments \( (\mu_{y}') \), its effect on the mesophase stability, the poorly linear dependencies of \( \sqrt{T_C} \) on \( \mu_{y}' \) (Figure 8), is positive for \( n = 6 \) and becomes negative for other alkyo-chain lengths; the 4-substituted analogues are always of higher mesophase stability than the lateral ones. With respect to the dipolar anisotropy \( (\Delta \mu, \text{ Figure 9}) \), the correlations parallel those with \( \mu_{y}' \), that is with negative slopes for the homologues, \( n = 6 \), and positive ones with the higher homologues.

3.5. Entropy changes upon lateral substitution

In a study conducted by Imerie [7] on laterally substituted dimeric liquid crystals possessing flexible spacer, it was difficult to interpret the observed decrease unambiguously, although it presumably reflects, in part, that the increase in biaxiality of the mesogenic groups resulted in flexible spacer being less strongly anchored at its ends and, thus, the data simply reflected a decrease in the interaction strength parameter of the core resulting from a reduction in the degree of conjugation. In a more recent investigation,[8] the values of \( \Delta S_{N-S} \) for cholesteryl-based liquid crystal dimers containing –S–S– link were found to be very small which could be attributed to the increased molecular biaxiality arising from the C–S–S–C dihedral angle. It was
Figure 7. Dependence of $\sqrt{T_C}$ on the lateral component of bond moment ($\mu'_x$) for compounds Ina-k.

Figure 8. Dependence of $\sqrt{T_C}$ on the longitudinal component of bond moment ($\mu'_y$) for compounds Ina-k.
observed \[8\] that $\Delta S_{N-I}/R$ values are considerably lower than that normally seen for liquid crystal dimers containing two mesogenic units attached via short unsaturated linkages, such as $\text{-CH=CH-}$, $\text{-CH=N-}$, or $\text{-N=N-}$. Hence, biaxiality do not apply to our group of investigated compounds, $\text{In}_{a-k}$, since all derivatives are linear, rod-shaped, molecules possessing no flexible spacer, their melting temperatures vary irregularly with the number of carbon atoms (only even numbers) in the terminal alkoxy chain, $n$, and so do the $\Delta S_{N-I}/R$ values, for all transitions, with $n$ (see Table 6). As can be seen from Table 6, $\Delta S_{C-I}/R$ varies irregularly either with the position of substituent or $n$.

Table 6. Transition entropies ($\Delta S/ R$) of the azo/esters, $\text{In}_{a-k}$.

| Compound no. | $n$ | X   | Cr-N | A-N | A-I | N-I |
|--------------|-----|-----|------|-----|-----|-----|
| $\text{I}_6$ | 6   | 2-CH$_3$ | –    | 28.3 | –    | –    | 1.20 |
| $\text{I}_6$ | 3-CH$_3$ | 29.5 | –    | 0.91 | 0.39 | –    |
| $\text{I}_6$ | H   | 26.9 | –    | 2.49 | –    | 1.67 |
| $\text{I}_6$ | 2-F | 17.5 | –    | 0.49 | –    | 1.53 |
| $\text{I}_6$ | 3-F | 13.8 | –    | 0.28 | –    | 2.34 |
| $\text{I}_6$ | 2-Br | –   | 14.3 | –    | –    | 1.09 |
| $\text{I}_6$ | 3-Br | –   | 29.5 | –    | –    | 1.06 |
| $\text{I}_6$ | 3-CN | –   | 8.51 | –    | –    | 1.12 |
| $\text{I}_8$ | 8   | 2-CH$_3$ | 28.3 | –    | –    | 0.62 |
| $\text{I}_8$ | 3-CH$_3$ | 24.8 | –    | 0.34 | –    | 1.55 |
| $\text{I}_8$ | H   | 13.5 | –    | 0.44 | –    | 0.31 |
| $\text{I}_8$ | 2-F | 9.25 | –    | 0.37 | –    | 0.14 |
| $\text{I}_8$ | 3-F | 6.47 | –    | 0.58 | –    | 1.44 |

(Continued)
Eight series of 2- (and 3-) substituted phenyl 4′-(4″-alkoxy phenylazo) benzoates were prepared and their thermal behaviour characterised. Two types of substituent were used, namely an alkoxy group of varying length and a small compact polar group, X. A comparison was made between the present series and the previously investigated 4-substituted isomers. The results were discussed in terms of polarity and steric effects. The study revealed that the stability of the mesophase is but poorly correlated with either the dipolar anisotropy of the whole molecular structure or with the dipolar anisotropy of the substituent, indicating that the dipole moment is not only the sole factor affecting mesophase stability; in addition, strong steric interaction upon lateral substitution is of concern. For constant alkoxy-chain length ($n$), a comparison was made between the stability of the mesophase of the three isomers bearing the same substituent but occupying different position (2-, 3- and 4-), and another between analogues bearing different polar groups attached to one and the same position. Both comparisons revealed that no one order of decrease in the mesophase stability is applicable for all values of $n$, indicating that the length of the alkoxy chain has a significant role that directs both conformation and steric effect.

### 4. Conclusions

Eight series of 2- (and 3-) substituted phenyl 4′-(4″-alkoxy phenylazo) benzoates were prepared and their thermal behaviour characterised. Two types of substituent were used, namely an alkoxy group of varying length and a small compact polar group, X. A comparison was made between the present series and the previously investigated 4-substituted isomers. The results were discussed in terms of polarity and steric effects. The study revealed that the stability of the mesophase is but poorly correlated with either the dipolar anisotropy of the whole molecular structure or with the dipolar anisotropy of the substituent, indicating that the dipole moment is not only the sole factor affecting mesophase stability; in addition, strong steric interaction upon lateral substitution is of concern. For constant alkoxy-chain length ($n$), a comparison was made between the stability of the mesophase of the three isomers bearing the same substituent but occupying different position (2-, 3- and 4-), and another between analogues bearing different polar groups attached to one and the same position. Both comparisons revealed that no one order of decrease in the mesophase stability is applicable for all values of $n$, indicating that the length of the alkoxy chain has a significant role that directs both conformation and steric effect.

### Disclosure statement

No potential conflict of interest was reported by the authors.

### Supplemental data

Supplemental data for this article can be accessed here.

### References

[1] Dewar MJS, Goldberg RS. Effects of central and terminal groups on nematic mesophase stability. J Org Chem. 1970;35:2711–2715. doi:10.1021/jo00833a051.

[2] Schroeder JP, Bristol DW. Liquid crystals. IV. Effects of terminal substituents on the nematic mesomorphism of p-phenylene dibenzoates. J Org Chem. 1973;38:3160–3164. doi:10.1021/jo00958a018.

[3] Hogan JL, Imrie CT, Luckhurst GR. Asymmetric dimeric liquid-crystals – the preparation and properties
of the alpha-(4-cyanobiphenyl-4'-oxy)-omega-(4-normal alkyl aniline benzylidene -4'-oxy) hexanes. Liq Cryst. 1988;3:645–650. doi:10.1080/0267829880866408.

[4] Attard GS, Date RW, Imrie CT, et al. Nonsymmetrical dimeric liquid- crystals – the preparation and properties of the alpha-(4-cyanobiphenyl-4'-yloxy)-omega-(4-alkylanilinobenzylidene -4'-oxy) alkanes. Liq Cryst. 1994;16:529–581. doi:10.1080/0267829940836531.

[5] Imrie CT. Non-symmetric liquid crystal dimers: how to make molecules intercalate. Liq Cryst. 2006;33:1449–1485. doi:10.1080/02678290601140498.

[6] Imrie CT, Henderson PA, Seddon JM. Non-symmetric liquid crystal trimers. First example triply-intercalated alternating smectic C phase. J Mater Chem. 2004;14:2486–2488.

[7] Imrie CT. Laterally substituted dimeric liquid-crystals. Liq Cryst. 1989;6:391–396. doi:10.1080/02678298908034184.

[8] Lee H-C, Lu Z, Henderson PA, et al. Cholesteryl-based liquid crystal dimers containing a sulfur-sulfur link in the flexible spacer. Liq Cryst. 2012;39:259–268. doi:10.1080/02678292.2011.641753.

[9] Gray GW. Molecular structure and the properties of liquid crystals. London: Academic Press; 1962. p. 239–298.

[10] Demus D, Goofby J, Gray GW, et al. Handbook of liquid crystals. Weinheim: Wiley-VCH; 1998. Vol. I, p. 151–153.

[11] Hird M, Toyne KJ, Gray GW, et al. The relationship between molecular structure and mesomorphic properties of 2,2'- and 3,2'-difluoroterphenyls synthesized by palladium-catalysed cross-couplings. Liq Cryst. 1995;18:1–11. doi:10.1080/02678299508036584.

[12] Sugiuira H, Sakurai Y, Masuda Y, et al. The substituent effect on mesomorphic properties of 4-oclyoxyphenyl 4-(4-R-3-nitrobenzoxallybenzoates and 4-(4-oclyoxybenzoxallybenzophenyl 4-R-3-nitrobenzoates. Liq Cryst. 1991;9:441–450. doi:10.1080/02678299910804577.

[13] Masuda Y, Sakurai Y, Sugiuira H, et al. The effect of a lateral substituent on the mesomorphic properties of 4-cyanophenyl 4-(4-alkoxybenzoxallybenzoates. Liq Cryst. 1991;10:623–634. doi:10.1080/02678299108241730.

[14] Dabrowski R, Bezborodov VS, Lapanik VJ, et al. Mesomorphic properties of phenyl 4-(5-alkyl-1,3,2-dioxaborin-2-yl) benzoates Influence of terminal and lateral substitution. Liq Cryst. 1995;18:213–218. doi:10.1080/02678299508036616.

[15] Kozlovsy MV, Shibaev VP, Stakhkovain AV, et al. A new approach to photorecording based on hindering a phase transition in photochromic chiral liquid crystal polymers. Liq Cryst. 1998;24:759–767. doi:10.1080/026782998206885.

[16] Prasad V. Liquid crystalline compounds with V-shaped molecular structures: synthesis and characterization of new azo compounds. Liq Cryst. 2001;28:145–150. doi:10.1080/026782901462481.

[17] Ruslim C, Ichimura K. Z-isomers of azobenzenes highly compatible with liquid crystals. Chem Lett. 1998;8:789–790. doi:10.1246/cl.1998.789.

[18] Shibaev VP, Kostomin SA, Ivanov SA. Comb-shaped polymers with mesogenic side groups as electro and photooptical active media. In: Shibaev VP, editor. Polymers as electrooptical and photooptical active media. Berlin: Springer; 1996. p. 37–110.

[19] Herman DS, Rudquist P, Ichimura K, et al. Flexoelectric polarization changes induced by light in a nematic liquid crystal. Phys Rev E. 1997;55:2857–2860. doi:10.1103/PhysRevE.55.2857.

[20] Sasaki T, Ikeda T, Ichimura K. Photochemical control of properties of ferroelectric liquid crystals. Photochemical flip of polarization. J Am Chem Soc. 1994;116:625–628. doi:10.1021/ja00081a024.

[21] Naoum MM, Fahmi AA, Ahmed NH, et al. The effect of inversion of the ester group on the mesophase behavior of some azoester compounds. Liq Cryst. Forthcoming 2015.

[22] Cmengena HK, Eysel W, Gmelin E, et al. The temperature calibration of scanning calorimeters. Thermochim Acta. 1993;219:333–342. doi:10.1016/0040-6031(93)80510-H.

[23] Lutfur MR, Hegde G, Kumar S, et al. Synthesis and characterization of bent-shaped azobenzene monomers: Guest–host effects in liquid crystals with azo dyes for optical image storage devices. Opt Mater. 2009;32:176–183. doi:10.1016/j.optmat.2007.09.006.

[24] Lutfur MR, Asik J, Kumar S, et al. Liquid crystalline banana-shaped monomers derived from 2,7-naphthalene: synthesis and properties. Liq Cryst. 2008;35:1263–1270. doi:10.1080/02678290802513808.

[25] Danietz D, Bauer M. Chromophoric poly(vinyl alcohol derivative)s. 1. Synthesis and spectroscopical characterization of some poly(vinyl alcohol)s with alkoxayazonenecarbonyl substituents. Makromol Chem. 1991;192:2635–2640. doi:10.1002/macp.1991.021921109.

[26] Liu M, Lutfur MR, Surugau NL, et al. Synthesis and characterization of ethyl cellulose–based liquid crystals containing azobenzene chromophores. Mol Cryst Liq Cryst. 2010;528:64–73. doi:10.1080/02678292.2010.504516.

[27] Naoum MM, Fahmi AA, Alaaasr MA, et al. Effect of lateral substitution of different polarity on the mesophase behavior in pure and mixed states of 4-(4-substituted phenylazo)-2-substitutedphenyl-4'-alkoxy benzoates. Liq Cryst. 2011;38:391–405. doi:10.1080/02678292.2010.550069.

[28] Naoum MM, Saad GR, Nessim RI, et al. Effect of molecular structure on the phase behavior of some liquid crystalline compounds and their binary mixtures. II. 4-Hexacecloyloxy phenyl arylates and aryl 4-hexadecyloxyarylates. Liq Cryst. 1997;23:789–795. doi:10.1080/026782997207713.

[29] Saad GR, Nessim RI. Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures VII[1]. The effect of molecular length. Liq Cryst. 1999;26:629–636. doi:10.1080/026782999204679.

[30] Yeap GY, Lee HC, Mahmoud WAK, et al. Synthesis, thermal and optical behavior of non-symmetric liquid crystal dimers σ-(4-benzylidene-substituted aniline-4-oxy)-o-pentyl-4-(4'-phenyl)benzoxide hexane.
[31] Yeap G-Y, Ha Seap T, Boey P-L, et al. Synthesis and Characterization of some new mesogenic Schiff base ester N-[4-(4-n-hexadecanoyloxy)benzylidene]=4-substitued anilines. Mol Cryst Liq Cryst. 2006;452:73–90. doi:10.1080/15421400500382156.

[32] Collings PJ. Liquid crystal: nature’s delicate phase of matter. Bristol: IOP Publishing; 1990.

[33] van der Veen J. The influence of terminal substituents upon the nematic-isotropic transition temperature. J Phys Colloque. 1975;36:375–377.

[34] Naoum MM, Saad GR, Nessim RI, et al. Effect of molecular structure on the phase behavior of some liquid crystalline compounds and their binary mixtures. IV. Dependence of $T_c$ on the anisotropy of polarizability of the aryl-X-bond. Liq Cryst. 1998;25:73–83. doi:10.1080/0267829980206515.