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# Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures XIII. 4-(4-Substituted phenylazo)phenyl 4-alkoxybenzoates

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# Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their mixtures

## XIII. 4-(4-Substituted phenylazo)phenyl 4-alkoxybenzoates†

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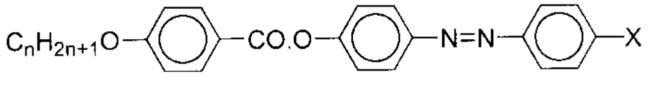
Five homologous series of 4-(4-substituted phenylazo)phenyl 4-alkoxybenzoates (**Ia–e**) were prepared in which the substituent ($X$) was taken from $CH_3O$, $CH_3$, Cl, $NO_2$, and CN, while, within each homologous series, the length of the terminal alkoxy group varied between 6 and 16 carbon atoms. Compounds prepared were characterized by infrared spectroscopy, and their mesophase behaviour investigated by differential scanning calorimetry and polarizing optical microscopy. The results are discussed in terms of mesomeric and polarizability effects. In each group of compounds bearing the same alkoxy group, the mesophase – isotropic transition temperatures ($T_c$) were successfully correlated with the polarizability anisotropy of bonds to the substituent $X$.

## 1. Introduction

In previous studies in this laboratory, the effect of a small compact terminal substituent ($X$) and an alkoxy terminal group of variable chain length on the mesophase behaviour of phenyl benzoate compounds [2], as well as of the 1,4-phenylene bis (benzoates) [3] based materials was investigated. In the former group of compounds [2], not all of the derivatives are mesomorphic, and the inversion of the ester group led to a significant variation in their mesophase behaviour. In the latter group [3], the introduction of the second $C_6H_5COO$ group to the phenyl benzoate molecule yielded compounds that are all mesomorphic and possess high melting ($T_m$) and clearing ($T_C$) temperatures, indicating the existence of strong attractive intermolecular forces both in the solid and in the mesophases. In both cases, the terminal substituents affected the polarizability of the aromatic rings to which they are attached to varying extents. As the polarity of the substituent increases, the clearing point ($T_C$) increases also. Van der Veen [4] proposed an equation that relates the clearing temperature ($T_C$) to the polarizability anisotropy ($\Delta\alpha_X$) of bonds ($C_{ar}$–$X$) to small compact substituents, (see § 3.2).

The goal of the present study is first to prepare series of model compounds of type **I**, in which a phenylazo group is introduced to the mesogenic portion of the substituted phenyl benzoate molecule; the effect of the polarity of the terminal substituent $X$, as well as the length of the alkoxy chain, on the stability of the liquid crystalline phase can then be investigated. Secondly, it is to test the relationship derived by van der Veen [4], and modified by Naoum [5], to the prepared compounds.



$\mathbf{I}_{a\text{-}e}$

**I6**, $n=6$; **I8**, $n=8$; **I10**, $n=10$; **I12**, $n=12$; **I14**, $n=14$; **I16**, $n=16$ **a**, $X=CH_3O$; **b**, $X=CH_3$; **c**, $X=Cl$; **d**, $X=NO_2$; **e**, $X=CN$.

Substituents were chosen to cover a wide range of electronic and dipolar characteristics, and the length of the alkoxy group varied between 6 and 16 carbon atoms.

## 2. Experimental

Chemicals were purchased from: Aldrich, Wisconsin, USA; E. Merck, Darmstadt, Germany; and Fluka, Buchs, Switzerland.

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†For part XII, see reference [1].

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### 2.1. *Preparation of Materials*

#### 2.1.1. *4-n-Alkoxybenzoic acids*

Ethyl 4-*n*-alkoxybenzoates were first prepared from ethyl 4-hydroxybenzoate and the appropriate 1-bromo-*n*-alkane; the esters were then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described previously [2]. The resulting acids were TLC pure and exhibited phase transition temperatures which agreed with those reported in the literature [6].

#### 2.1.2. *4-(4-Substituted phenylazo)phenol*

One molar equivalent of the 4-substituted aniline in ice-cold dilute hydrochloric acid was diazotized with cold sodium nitrite solution and then added dropwise to a cold phenol/NaOH (1/1) solution. The solid product was filtered off and recrystallized twice from glacial acetic acid. The resulting azo dyes were TLC pure and exhibited melting temperatures in agreement with those reported in [7].

#### 2.1.3. *4-(4-Substituted phenylazo)phenyl 4-alkoxybenzoates (**Ia–e**)*

One molar equivalent of the 4-(4-substituted phenylazo)phenol and 4-*n*-alkoxybenzoic acid were dissolved in methylene dichloride. To the resulting solution, dicyclohexyl carbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) were added and the solution left to stand overnight at room temperature with stirring. The solvent was then distilled off and the residue crystallized from ethanol. The product was TLC pure, and the elemental analyses of new derivatives agreed with expected structures.

### 2.2. *Physical characterization*

Calorimetric investigations were made using a Polymer Laboratories (England) differential scanning calorimeter, PL-DSC, with nitrogen as a purge gas. The instrument was calibrated from the melting points of ultra-pure metals, and a value of $28.45\,\mathrm{J\,g^{-1}}$ was used for the enthalpy of fusion of indium. The typical heating rate was $10\,\mathrm{K\,min^{-1}}$, and a sample mass was 2–3 mg. Transition temperatures were identified with a standard polarized-light microscope (C. Zeiss, Germany), attached to an FB 52 hot-stage equipped with an FB 80 central processor (Mettler, Switzerland).

Thin layer chromatography was performed with TLC sheets coated with silica gel (E. Merck); spots were detected by UV irradiation. Silica gel (No. 6634, E. Merck) was used for column chromatography.

## 3. Results and discussion

Infrared spectra and elemental analyses for the newly prepared derivatives were found to be consistent with the structures assigned. Infrared absorption bands of the ester carbonyl group revealed that neither the length of the alkoxy group, $C_6$–$C_{16}$, in any of the homologous series, **Ia–e**, nor the substituent *X*, in any series bearing the same alkoxy group, has a significant effect on the absorption associated with the carbonyl group. Transition temperatures, as measured by DSC, and the phases identified by polarizing-optical microscopy for all compounds investigated are summarized in table 1.

### 3.1. *DSC analyses*

In order to investigate the effect of the terminal substituents (*R* and *X*) on the mesophase behaviour of the compounds prepared, the number of carbon atoms in the substituent *R* was kept constant (at 6, 8, 10, 12, 14 or 16), while the other substituent *X* varied between $CH_3O$, $CH_3$, Cl, $NO_2$, and CN. Table 1 compares

Table 1. Transition temperatures (in °C) for compounds $4\text{-}C_nH_{2n+1}O\text{–}C_6H_4\text{–}COO\text{–}C_6H_4\text{–}N\text{–}N\text{–}C_6H_4\text{–}X\text{–}4$.

| Compound | *n* | *x* | $T_{C\text{–}A}$ | $T_{C\text{–}N}$ | $T_{A\text{–}N}$ | $T_{A\text{–}I}$ | $T_{N\text{–}I}$ | Ref. |
|---|---|---|---|---|---|---|---|---|
| **I6a** | 6 | $CH_3O$ | — | 122.8 | — | — | 255.8 | [8] |
| **I6b** | | $CH_3$ | — | 103.5 | — | — | 227.8 | [8] |
| **I6c** | | Cl | 114.9 | — | 145.6 | — | 241.0 | [9] |
| **I6d** | | $NO_2$ | 103.6 | — | 240.5 | — | 254.7 | — |
| **I6e** | | CN | 110.0 | — | 151.8 | — | 266.4 | [10] |
| **I8a** | 8 | $CH_3O$ | — | 117.9 | — | — | 233.5 | [8] |
| **I8b** | | $CH_3$ | — | 107.5 | — | — | 208.9 | [8] |
| **I8c** | | Cl | 107.6 | — | 179.3 | — | 224.2 | [9] |
| **I8d** | | $NO_2$ | 99.9 | — | 237.9 | — | 249.9 | — |
| **I8e** | | CN | 93.0 | — | 191.7 | — | 257.5 | [10] |
| **I10a** | 10 | $CH_3O$ | — | 137.8 | — | — | 220.9 | — |
| **I10b** | | $CH_3$ | — | 105.0 | — | — | 188.1 | — |
| **I10c** | | Cl | 123.9 | — | — | 210.9 | — | [9] |
| **I10d** | | $NO_2$ | 102.6 | — | — | 230.9 | — | — |
| **I10e** | | CN | 105.1 | — | 223.0 | — | 243.5 | [10] |
| **I12a** | 12 | $CH_3O$ | — | 130.7 | — | — | 209.3 | — |
| **I12b** | | $CH_3$ | — | 98.9 | — | — | 183.9 | — |
| **I12c** | | Cl | 120.1 | — | — | 197.7 | — | [9] |
| **I12d** | | $NO_2$ | 86.5 | — | — | 221.9 | — | — |
| **I12e** | | CN | 93.6 | — | 228.0 | — | 232.0 | [10] |
| **I14a** | 14 | $CH_3O$ | — | 114.6 | — | — | 196.7 | — |
| **I14b** | | $CH_3$ | — | 96.1 | — | — | 179.9 | — |
| **I14c** | | Cl | 104.3 | — | — | 193.4 | — | — |
| **I14d** | | $NO_2$ | 93.5 | — | — | 215.3 | — | — |
| **I14e** | | CN | 98.4 | — | — | 226.6 | — | — |
| **I16a** | 16 | $CH_3O$ | — | 124.2 | — | — | 192.1 | — |
| **I16b** | | $CH_3$ | — | 98.8 | — | — | 170.6 | — |
| **I16c** | | Cl | 105.3 | — | — | 186.0 | — | — |
| **I16d** | | $NO_2$ | 101.8 | — | — | 210.9 | — | — |
| **I16e** | | CN | 97.3 | — | — | 220.7 | — | 10 |

the transition temperatures of these six groups of derivatives.

It is well known that the stability of the mesophase would be augmented by an increase in the polarity or polarizability of the mesogenic part of the molecule. The relative strength of the lateral and terminal cohesive forces between molecules determines the type of the mesophase formed [11]. Strong lateral and weak terminal intermolecular cohesions will give rise to a smectic mesophase, which, if the lateral cohesions are high enough, may persist until the isotropic liquid is formed [11]. Thus, in the cyano (or nitro) analogues the mesomeric interaction between the alkoxy oxygen and the ester carbonyl, on one side of the molecule, is augmented by the conjugative interaction between the ester oxygen and the CN (or $NO_2$) group via the phenylazo benzene group, on the other side of the molecule (figure 1). This should increase the polarity of the mesogenic portion as a whole, which stabilizes the mesophase. This inference is in accordance with the experimental results (table 1) that the cyano and nitro analogues have the highest clearing ($T_C$) temperatures.

Conversely, there are opposing effects on each side of the molecules of the methoxy (**Ia**) and methyl (**Ib**) analogues (figure 2). Accordingly, they are expected to possess lower dipolar character that would lead to derivatives with lower $T_C$ values.

As can also be noted from table 1, all homologues of the methoxy and methyl substituted derivatives exhibit only the nematic mesophase. The chloro, nitro and cyano compounds gave either a single smectic mesophase for higher homologues, or a smectic followed by a nematic mesophase at higher temperatures, for shorter homologues. The substituents *X* attached to the mesomorphic compounds can be placed in the order of enhancing either nematic or smectic phase stability.

(*a*) The nematic thermal stability decreases in the order:

$$CN > NO_2 > CH_3O > Cl > CH_3$$

for all series except for the **I6** analogues, where the order $NO_2 > CH_3O$ is inverted. This latter order with the $NO_2 > CH_3O$ inversion is the same as that given in the nematic terminal group efficiency order for a much wider range of substituents in a number of different mesogenic anils and other systems first reported by Gray and later extended [11].

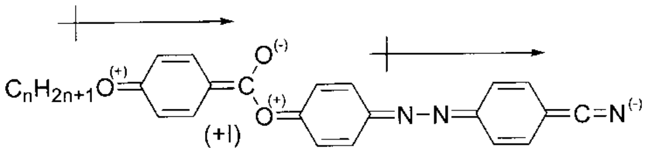


Figure 1. Conjugative interactions in the cyano (or nitro) substituted derivatives.

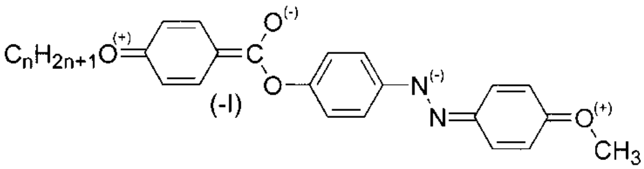


Figure 2. Conjugative interactions in the methoxy substituted derivatives.

(*b*) The group efficiency order for smectic phase stability is:

$$NO_2 > CN > Cl \quad \text{for } \mathbf{I6-I10}, \text{ and}$$

$$CN > NO_2 > Cl \quad \text{for } \mathbf{I12-I16}.$$

The methoxy and methyl homologues are only nematogenic. This implies that these substituents lie below Cl in the order.

As noted again by Gray, a consistent smectic group efficiency order for terminal substituents is much less obvious, and the above order differs considerably from that which he found for a few systems, namely:

$$Cl > NO_2 > CH_3 > H > CH_3O.$$

It is evident therefore that, whilst very similar orders for the effect of terminal groups on nematic thermal stability exist for a range of systems, this is not the case for the thermal stability of more ordered smectic phases where more intimate and variable intermolecular steric contacts must affect the situation, in addition to factors such as conjugative effects, dipole interactions and the overall polarizability of the system. As a result a given substituent may have different effects when it is present in different smectogenic systems.

In order to investigate the effect of increasing the alkoxy chain length, on phase behaviour, for a homologous series, the transition temperatures are plotted in figure 3 for each homologous series against the length of the alkoxy group (*n*), with the remaining part of the molecule held constant. These plots show that, irrespective of the substituent *X*, the mesophase–isotropic transition temperatures ($T_C$) decrease regularly with increasing alkoxy chain length. These results are in accord with previous observations [11, 12]. A common pattern of behaviour, revealed in figure 3, is that the nematic–isotropic transition temperatures fall with increasing chain length. In series that also exhibit smectic properties (i.e. **Ic–e**), the smectic–nematic transition temperatures were found to rise steeply at first and then more gradually as the alkoxy chain lengthens. The smectic–nematic curve becomes coincident

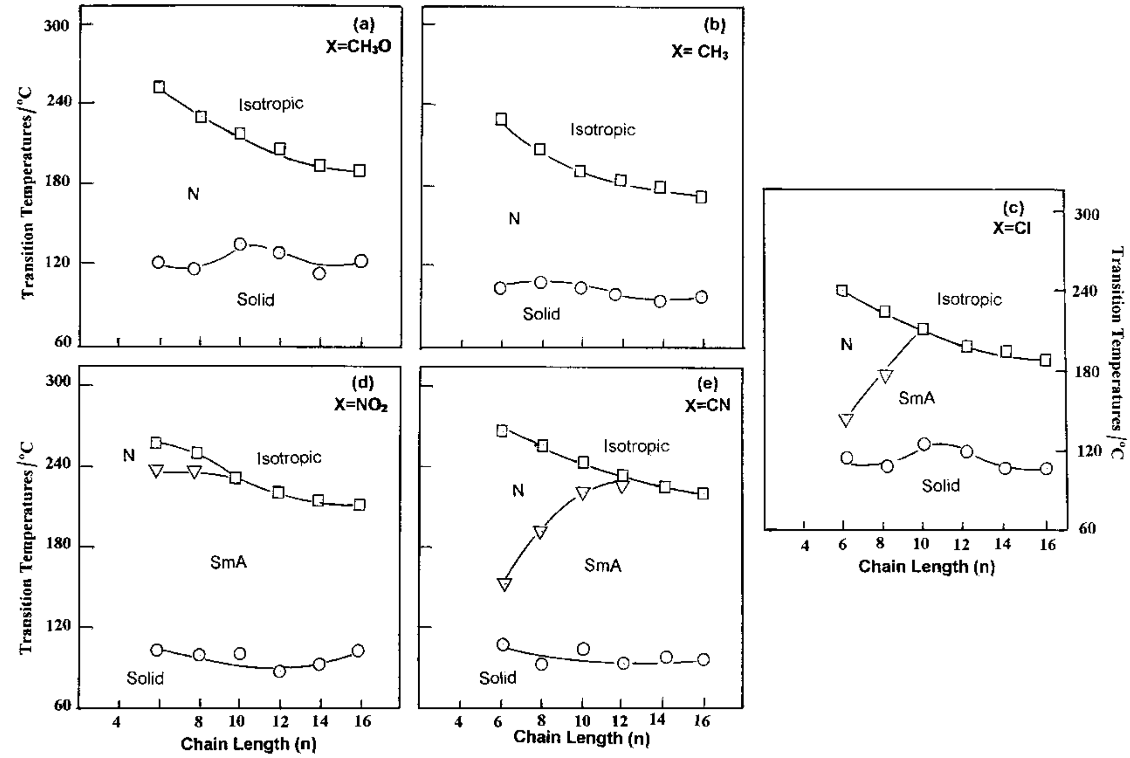


Figure 3. Dependence of the transition temperatures of compounds **(I6–I16)$_{a–e}$** on the alkoxy chain length (*n*).

with the falling nematic–isotropic curve before the former has reached its maximum. After these two curves have merged, no nematic properties are observed in the series, and the smectic mesophase passes directly to the isotropic liquid. These smectic–isotropic transitions begin at about the decyl (for the chloro, **Ic**, and nitro, **Id**) or dodecyl (for the cyano, **Ie**) homologues. Such behaviour is in accord with that reported by Gray [11] whereby 44 of the 70 homologous series studied behaved in this general way. As the alkyl chain is lengthened, the separation of the aromatic centres, which are highly polarizable and carry the dipolar substituent *X*, is increased, and there should be a relative decrease in the strength of the terminal intermolecular cohesive interactions [11]. However, the addition of a methylene group increases the overall polarizability of the molecule [13]; consequently the lateral intermolecular attractions increase, as the chain length grows.

### 3.2. *Clearing temperatures and polarizability anisotropy of $C_{ar}$–X bonds*

The relationship derived by van der Veen [4], between the stability of the mesophase in a liquid crystalline compound, expressed as the clearing temperature, $T_C$ (in K), and the anisotropy of polarizability, $\Delta\alpha_X$, of bonds to small compact terminal substituent ($C_{ar}$–*X*), has the form:

$$T_C \propto \left(\Delta\alpha_M{}^2 + 2\Delta\alpha_M\Delta\alpha_X + \Delta\alpha_X{}^2\right) \qquad (1)$$

where $\Delta\alpha_M$ is the polarizability anisotropy for the molecular structure except the terminal substituent, *X*. Equation (1) can be expressed in the form:

$$T_C^{\frac{1}{2}} \propto (\Delta\alpha_M + \Delta\alpha_X) = a.\Delta\alpha_M + a.\Delta\alpha_X \qquad (2)$$

where $a$ is a proportionality constant. Thus, if $T_C^{\frac{1}{2}}$ is plotted against $\Delta\alpha_X$ for each series of liquid crystalline compounds with the same alkoxy group, i.e. **I6–I16**, a straight line is expected with slope $a$ and intercept $a.\Delta\alpha_M$. The polarizability anisotropy, $\Delta\alpha_M$, for the molecular structures excluding the terminal substituent *X*, is thus given by:

$$\Delta\alpha_M = \text{intercept/slope}. \qquad (3)$$

The values of $T_C^{\frac{1}{2}}$ were plotted against $\Delta\alpha_X$, as calculated previously [5], for the six series **I6–I16**; the plots are shown in figure 4. In this manner, the slopes and intercepts were calculated for each regression line, in figure 4, by the methods of least squares, from which $\Delta\alpha_M$ could be calculated, for the six series of compounds; the results are given in table 2.

Plotting $\Delta\alpha_M$ values as a function of the number of carbon atoms in the alkoxy chain gave a straight line

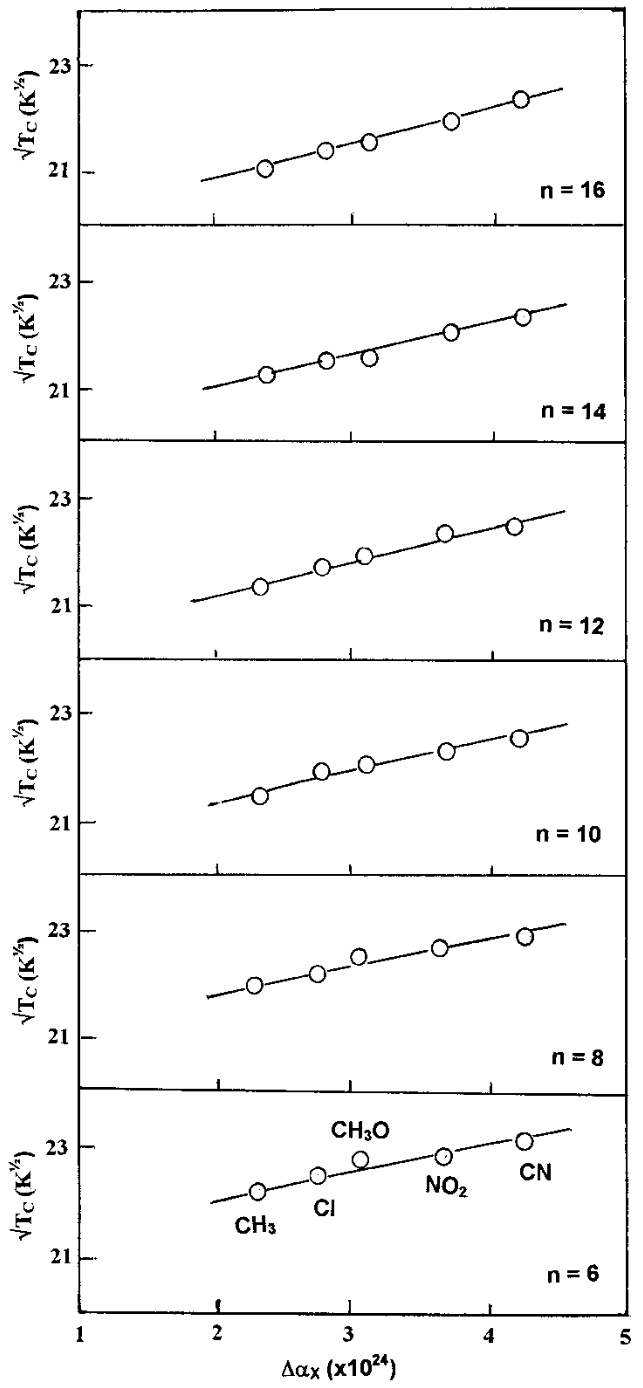


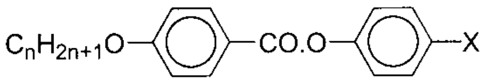
Figure 4. Dependence of $T_C$ on the polarizability anisotropy, $\Delta\alpha_X$, of the $C_{ar}$–$X$ bonds.

with slope $=-7.95\times10^{21}$ and intercept $=4.44\times10^{23}$. The results revealed that the polarizability anisotropy of the molecule, excluding the substituent *X*, decreases linearly as the alkoxy chain is lengthened. This reflects the decrease in the molecular rigidity and polarity of the molecule as a result of increasing *n*-alkane character.

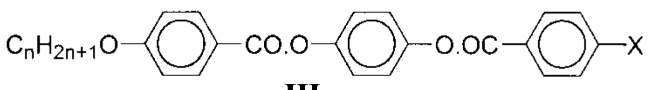
Table 2. Slopes and intercepts of regression lines and the $\Delta\alpha_M$ values for the **I6**–**I16** series.

| Series | *n* | Slope ($\times10^{-23}$) | Intercept $K^{1/2}$ | $\Delta\alpha_M\times10^{23}$ $Cm^3$ |
|---|---|---|---|---|
| **I6** | 6 | 5.33 | 21.10 | 3.96 |
| **I8** | 8 | 5.46 | 20.70 | 3.79 |
| **I10** | 10 | 5.59 | 20.30 | 3.63 |
| **I12** | 12 | 5.77 | 20.10 | 3.48 |
| **I14** | 14 | 5.99 | 19.90 | 3.32 |
| **I16** | 16 | 6.23 | 19.70 | 3.16 |

The nature and length of the central mesogenic group are also of great importance. This can be studied by comparing compounds, **Ia–e**, with the corresponding substituted 4-aryl-4′-alkoxybenzoates [13], **IIa–e**, and 1,4-phenylene-bis-4′-substituted benzoates [3], **IIIa–e**, with respect to the crystal–mesophase ($T_m$) and mesophase–isotropic ($T_C$) transition temperatures, as well as the mesomorphic ranges, $\Delta T=T_m$–$T_C$.



**IIa-e**



**IIIa-e**

Corresponding analogues in the three groups of compounds (**I**, **II**, and **III**) differ from each other in the mesogenic segment of the molecule, but they do contain the same substituents (*X* and *R*). The study revealed that the introduction of a phenylazo moiety into the phenyl benzoate molecule in **II** to form **I** results in an increase of the intermolecular forces, and consequently of the stability of the solid and mesophase; i.e. in an increase in the melting and clearing temperatures [14]. Furthermore, while the methoxy, methyl, and chloro substituted analogues of **II** showed monotropic mesophases, the corresponding analogues in series **I** showed enantiotropic mesophases with high clearing temperatures. On the other hand, replacement of the ester group in **III** [3] by an azo linkage in **I** has led to a decrease in $T_m$ and an increase in $T_C$; that is, compounds **I** have greater mesomorphic ranges than those of the corresponding analogues in series **III**.

Irrespective of the alkoxy chain length, the difference is marked in the case of the electron-withdrawing substituted chloro, nitro, and cyano analogues, and becomes smaller as the alkoxy chain is lengthened. These results can be explained in terms of two competitive effects: polarizability anisotropy and repulsive forces. The polarizability anisotropy ($\Delta\alpha_M$) of the whole molecular structure (excluding the substituent X), calculated for compounds of group **I**, as well as those reported previously for compounds **II** [14] and **III** [3] are collected in table 3. As can be seen from this table, $\Delta\alpha_M$ for compounds **I** and **III** decreases as the alkoxy chain is lengthened, whereas for compounds **II** the reverse is true. In the case of the phenyl benzoate molecule (compounds **II**), the increase in $\Delta\alpha_M$ with chain length reflects the increase in the lateral aliphatic–aliphatic interactions of the rod-shaped molecules, which adds to the dipole–dipole interactions, as a result of increasing the *n*-alkane character. Conversely, in the other two cases (**I** and **III**), the decrease in $\Delta\alpha_M$ reflects the decrease in molecular rigidity and polarity in both structures. It is also clear from table 3 that, irrespective of the alkoxy chain length, $\Delta\alpha_M$ decreases in the order: **II** > **I** > **III**. As mentioned earlier, an increase in the polarizability anisotropy increases the stability of the mesophase, as measured by the increase in $T_C$. This was found to be the case; that is $T_C$ decreases in the same order. Alternatively, in the more compact solid phase, as the polarizability of the molecule is increased, repulsive interactions dominate, resulting in less stable solids and lower melting points, as is observed.

## 4. Conclusions

4-(4-Substituted phenylazo)phenyl benzoates were prepared and their thermal behaviour characterized. Two types of substituent were used, namely, an alkoxy group of varying length and a small compact polar group, *X*. All the compounds investigated were found to possess high transition temperatures indicating strong intermolecular association either in the solid or mesophase. Conjugation between the alkoxy and ester carbonyl groups, on one side of the molecule, increases the polarity of the carbonyl oxygen and so stabilizes the mesophase. On the other side of the molecule, varying the electronic nature of the substituent *X* resulted in extremes in the electronic interactions between the substituent and the mesogenic part via the phenylazo group. Such differences have led to a significant variation in the mesophase behaviour of the compounds. The infrared spectra were consistent with these inferences.

Table 3. Polarizability anisotropy ($\Delta\alpha_M \times 10^{23}$ in C m$^3$) of the molecular structure, excluding substituent *X*, for compounds **I**, **II**, and **III**, as a function of alkoxy chain length (*n*).

| *n* | I | II | III |
|---|---|---|---|
| 6 | 3.96 | 4.02 | 3.39 |
| 8 | 3.79 | 4.42 | 3.20 |
| 14 | 3.32 | 5.01 | 2.64 |
| 16 | 3.16 | 5.22 | 2.46 |

In the nitro and cyano, and to a lesser extent the chloro analogues, the polarity of the molecule is augmented by the inductive withdrawing effect of the substituent, which helps to stabilize both the solid and mesophase. Conversely, the opposing effects on both sides of a molecule containing electron-donating ($CH_3O$ and $CH_3$) substituted derivatives results in fewer polar compounds that have relatively lower $T_m$ and $T_C$ values. Furthermore, the extension of the terminal *n*-alkoxy chain gives rise to a decrease in the mesophase–isotropic transition temperatures, suggesting that its effect becomes dominant over polarity variation. It was found that $T_C^{\frac{1}{2}}$ is linearly related to the polarizability anisotropy, of the $C_{ar}$–$X$ bond for all the series investigated.

Comparing the phase stability of the compounds reported here with the correspondingly substituted phenyl benzoates and 1,4-phenylene bis-(4-substituted)-benzoates revealed that introducing a phenylazo or PhCOO group into the phenyl benzoate molecule enhances the stability of the solid and mesophase. On the other hand, replacement of the PhCOO group by a phenylazo group enhances the stability of the mesophase and lowers the melting temperatures (i.e. increasing $\Delta T$), a property that can be further improved by investigating the mesophase behaviour in their binary mixtures; this will be reported elsewhere.

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