Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures. I. 4-Hexadecyloxyphenyl-4-carboxybenzoate and 4-carboxyphenyl-4-hexadecyloxybenzoate

Magdi M. Naoum; G. Hohne; H. Seliger; E. Happ

To cite this Article Naoum, Magdi M. , Hohne, G. , Seliger, H. and Happ, E.(1997) 'Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures. I. 4-Hexadecyloxyphenyl-4-carboxybenzoate and 4-carboxyphenyl-4-hexadecyloxybenzoate', Liquid Crystals, 23: 5, 653 — 658

To link to this Article: DOI: 10.1080/026782997207920

URL: http://dx.doi.org/10.1080/026782997207920

Liquid Crystals, 1997, Vol. 23, No. 5, 653–658

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures.
I. 4-Hexadecyloxyphenyl-4′-carboxybenzoate and 4-carboxyphenyl-4′-hexadecyloxybenzoate

by MAGDI M. NAOUM*
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

G. HOHNE
Section of Calorimetry and Spectroscopy, University of Ulm, D 89069 Ulm, Germany

H. SELIGER and E. HAPP
Section of Polymer, University of Ulm, D 89069 Ulm, Germany

(*Received 29 April 1997; accepted 19 June 1997*)

4-Hexadecyloxyphenyl-4′-carboxybenzoate (**A**) and 4-carboxyphenyl-4′-hexadecyloxy benzoate (**B**) were prepared and thermally characterized by polarized light microscopy and differential scanning calorimetry. Both compounds possess high transition temperatures indicating the formation of linear dimer molecules in the solid and liquid phases. The infrared data support the conclusion that the alkoxyphenyl carbonyl unit in **A** is more polarizable and hence stabilizes the intermolecular packing, thus leading to enhanced mesogenicity. Mixtures of the two compounds were prepared and thermally characterized to construct the phase diagram that showed a simple eutectic behaviour in the solid–mesophase transitions, and a linear mesophase–isotropic transition temperatures. The latter behaviour was attributed to similar electronic factors in both molecules.

1. Introduction

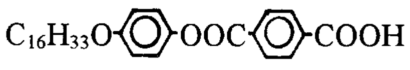
Liquid crystals form a state of matter intermediate between crystalline solids and isotropic liquids. Such mesophases behave mechanically as liquids, but differ from normal liquids in that molecules in them are oriented, having lost two degrees of freedom. The vast majority of mesogenic molecules are rod-shaped structures having a rigid central core. This core is often composed of aromatic rings joined through a linking group such as –COO, –CH=N–, or –N=NO– [1]. Aromatic esters are known [2] to be thermally stable and relatively resistant to hydrolysis. On the other hand, the favoured conformation of a compound such as phenyl benzoate should be one in which the aryl groups are *trans* to one another, in addition, conjugative interactions within the ester group and the benzene rings do lead to some double bond character and to a stiffer structure than might be expected. Thus, an obvious choice for our study seemed to be the arylates.

Liquid crystalline compounds and their mixtures offer a unique opportunity to examine structure–property relationships in their condensed phases. In general, binary mixtures of liquid crystalline materials exhibit eutectic behaviour in their crystalline–anisotropic transition temperatures, whereas their mesophase–isotropic transition temperatures vary linearly with composition [3]. However, Griffin and Johnson [4] reported that a binary mixture of 4-nitrophenyl-4′-decyloxybenzoate and 4-heptyloxybenzylidene-4′-butylamine exhibit smectic–isotropic transition temperatures, which are strongly non-linear with composition. It was found that these transitions were enhanced in regions of mixed compositions. These findings have been also observed by others and found to occur with a variety of systems [5–12].

Our objective in this work is to prepare and characterize, thermally and optically, the two isomeric esters, **A** and **B**, which differ only in the orientation of the –COO– group. These two compounds represent extremes in conjugative interactions between the terminal substituents, namely *R*O– and COOH groups, and the other portions of the molecule.

---

*Author for correspondence.



(**A**)

(**B**)

The other aspect of this investigation is to examine the mesophase behaviour in their binary mixtures.

2. Experimental

2.1. *Materials and analysis*

Chemicals were purchased from the following Companies: E. Merck, Darmstadt, Germany; Fluka, Buchs, Switzerland; and Aldrich, Wisconsin, U.S.A. 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. Infrared spectra were measured with a Perkin–Elmer B 25 spectrophotometer, ^{1}H NMR spectra with a Varian EM350L (60 Hz), and mass spectra with a Varian MAT 71. Calorimetric investigations were performed with a power compensated differential scanning calorimeter, Perkin–Elmer DSC7 with nitrogen as purge gas (20 ml min^{-1}). Typical heating rates were 10 K min^{-1}, and typical sample masses were 1–2 mg. Transition temperatures were determined with a standard polarized light microscope (C. Zeiss, Germany) attached to a FB52 hot-stage equipped with an FB80 central processor (Mettler, Switzerland).

2.2. *Phase diagrams*

Mixtures of the two components, in known proportions, were prepared by fusion, thoroughly mixed, and cooled in air to room temperature. Transition temperatures were determined both with the polarizing microscope and the DSC.

2.3. *Synthesis*

2.3.1. *Preparation of 4-hexadecyloxybenzoic acid*

This was prepared in 92 per cent yield from ethyl-4-hydroxybenzoate and 1-bromohexadecane by the method of Gray and Jones [13]. The ester was then saponified in ethanolic potassium hydroxide (95 per cent yield), and the resulting acid crystallized twice from glacial acetic acid, was TLC pure and exhibited the following phase transitions: $T_m = 102$°C, $T_c = 131$°C.

2.3.2. *Preparation of 4-hexadecyloxybenzoyl chloride*

It was prepared from the acid by heating with an excess of thionyl chloride under reflux for 5 h. The excess thionyl chloride was removed using a rotatory evaporator to give as a residue the crude acid chloride.

2.3.3. *Preparation of 4-hexadecyloxy phenol*

This was prepared in 65 per cent yield from hydroquinone monobenzyl ether and 1-bromohexadecane by the method described previously [14]. The benzyl ether linkage was then cleaved by hydrogenation, in chloroform solution, in the presence of Pd/C catalyst. The product was crystallized twice from ethanol to give TLC pure crystals that melted at 83·6°C [15].

2.3.4. *Preparation of 4-hexadecyloxyphenyl-4′ carboxybenzoate (***A***)*

This was prepared by a method described in previous work [15]. One molar equivalent of 4-hexadecyloxy phenol in dry pyridine was added dropwise to a solution of terephthaloyl chloride in pyridine over a period of 1 h, and the resulting mixture was heated overnight with stirring at 60°C. The product was column separated over silica gel using 10 per cent methanol/dichloromethane as the eluent, and finally crystallized from ethanol. Transition temperatures were determined by both polarizing microscope and differential scanning calorimetry.

2.3.5. *Preparation of 4-carboxyphenyl-4′ hexadecyloxybenzoate (***B***)*

It was prepared [15] by the reaction of benzyl-4-hydroxybenzoate with 4-hexadecyloxybenzoyl chloride in dry pyridine. The benzyl ester was then specifically cleaved by hydrogenation, under pressure and in presence of Pd/C as catalyst, of the chloroform solution. The product was crystallized twice from ethanol to give TLC pure crystals.

Infrared and mass spectra, elemental analyses, and NMR data for all compounds prepared were consistent with the structures assigned [15].

3. Results and discussion

The DSC curves for compounds **A** and **B** were measured in one case as solids crystallized from ethanol (first run), and in another case after being melted to 230°C and then cooled to room temperature (second run). The DSC curves are depicted in figures 1 and 2 for compounds **A** and **B**, respectively. Figures 1 and 2 show that for compound **A**, all transitions are reproducible, while for compound **B**, some changes were observed. To elucidate whether these changes in **B**, were due to chemical or physical transformation accompanying heating to 230°C, infrared spectra (in KBr) of compound **B**

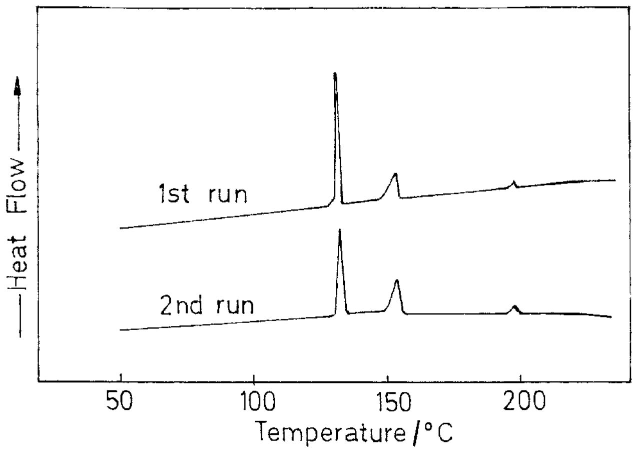


Figure 1. DSC thermograms for compound **A**.

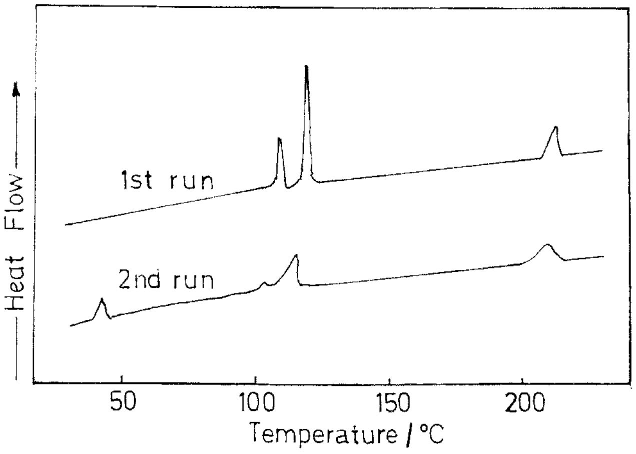
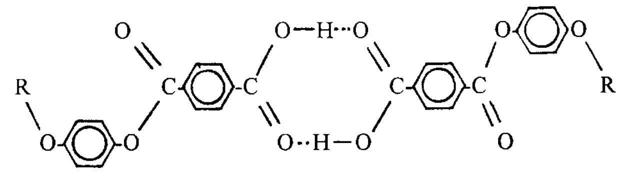


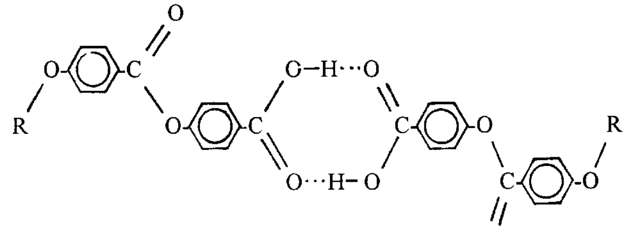
Figure 2. DSC thermograms for compound **B**.

were recorded for a sample crystallized from ethanol and another after being melted to 230°C for 15 min and then cooled to room temperature. A similar investigation was performed for compound **A** for the sake of comparison. The results revealed that both compounds **A** and **B** retained their characteristic bands but changes in the relative intensities of some bands were observed for compound **B**. The characteristic C=O bands, with their relative intensities and respective band width, are given in table 1.

Generally, the ester oxygen, as an electronegative atom, raises the C=O stretching frequency above that of a ketone. The carboxylic acid, on the other hand, in its condensed state (as in a pellet) tends to dimerize via hydrogen bonding [16]. This weakens the C=O bond resulting in a lowering of the carbonyl frequency of the acid, compared to its corresponding ester. This conclusion allows one to assign the higher frequency peaks, in table 1, to the ester C=O group and the lower ones to the acid C=O group, in both compounds.

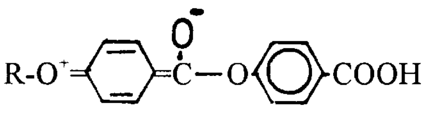


(A)



(B)

It can be seen from table 1 that compound **A** possesses an ester C=O that absorbs at a higher frequency than compound **B**. This may be attributed, in compound **B**, to the direct conjugation between the lone pair of electrons on the alkoxy oxygen, and the ester carbonyl group through the intervening aromatic ring [17, 18]. This increases the single bond character of the C=O bond, and hence, lowers its force constant, and consequently, its absorption frequency.



(B)

It can also be observed from table 1 that the characteristics of the two C=O bands of compound **A** do not change upon melting, while for compound **B**, small changes are observed in the intensity and band width for both C=O groups. These changes may be ascribed to changes in the crystalline structure in the solid phase that may affect the dipole–dipole interactions and/or hydrogen bond strength. This conclusion is evidenced by the appearance, in the second DSC run, of a new solid–solid endotherm, observed at 42·3°C, accompanied by a change in T_m from 109·8 to 103·5°C. Many polymorphic transitions [19] show considerable thermal hysteresis; this was attributed to differences between the volumes of the original and final phases and to strains in the lattice. A third DSC run was taken for compound **B** one month after the second run. The thermogram obtained was identical with the first one; this adds an extra evidence that only some crystalline modifications take place upon melting.

The assignments of transition temperatures were confirmed by polarized light microscopy. Transition temperatures obtained by the microscope agreed to within 2°C

Table 1. Characteristics of C=O stretching absorption frequencies of compounds **A** and **B**.

	C=O (ester)			C=O (acid)		
Compound	Frequency	Intensity	Band width	Frequency	Intensity	Band width
A (ethanol)	1741	93·9	18	1690	80·2	47
(melt)	1741	93·9	19	1690	80·4	48
B (ethanol)	1731	99·3	18	1689	87·5	40
(melt)	1733	93·8	24	1688	89·7	46

with values from DSC. The data obtained are given in table 2. It is customary to accept, as the transition temperature, the one obtained during the heating cycle since superheating is rare but supercooling is frequently observed.

Generally, the stability of a mesophase should be greater, the greater the lateral adhesion of the rod-shaped molecules in question, which, in turn, would be augmented by the increase in the polarity and/or the polarizability of the central part of the molecule. In 4-carboxyphenyl-4′-hexadecyloxybenzoate (**B**), as shown above, there is a mutual conjugation between the alkoxy oxygen and the ester C=O group, and this should increase the polarity of the carbonyl oxygen that helps to stabilize the mesophase ($\Delta T = 212{\cdot}4 - 119{\cdot}8 = 92{\cdot}6$°C). Alternatively, in the 4-hexadecyloxyphenyl-4′-carboxybenzoate (**A**), such mutual conjugation is lacking, in addition to the competitive interaction between the two C=O groups and the intermediate phenylene group, thus leading to a lower mesophase stability ($\Delta T = 217{\cdot}5 - 133{\cdot}8 = 83{\cdot}7$°C) for compound **A**.

One obvious way of achieving liquid crystallinity over a wide range of temperatures is to use eutectic mixtures of materials forming liquid crystals. If the molecules in question are similar in shape, the liquid crystalline–isotropic transition is usually a smooth line, and the temperature range of the liquid crystalline phase, consequently, is greater for the eutectic mixture than for either pure components. Our isomers **A** and **B** provide a very favourable example for this purpose. The phase diagrams, and the corresponding DSC thermograms, for our **A**/**B** system, constructed separately for the first and second DSC runs, are given in figures 3 and 4, respectively. The difference between the two diagrams are rather small and concern mostly the solid phase, particularly below the eutectic temperature (84°C) which is believed to be metastable and change to its original crystalline structure after some period of time. A mixture of this kind shows a relatively wide mesophase range ($\Delta T =$ 122°C) and has the advantage over materials, such as Schiff's bases or azoxy compounds, of being thermally and chemically stable. Also observed in figures 3 and 4, in the mixture composition range 40–90 mol % of **A**, was an exotherm which in many cases overlaps with the eutectic endotherm. These nucleation exotherms, observed between 80 and 100°C, are purely a kinetic problem and have nothing to do with the thermodynamic processes.

4. Conclusions

The two molecules 4-hexadecyloxyphenyl-4′-carboxybenzoate (**A**) and carboxyphenyl-4′-hexadecyloxybenzoate (**B**), which differ only in the location inversion of the ester group, were thermally characterized for their transition temperatures in the pure state and their binary mixtures. Both compounds possess high transition temperatures due to the formation of linear dimeric molecules in the solid and liquid phases. The greater mesophase stability of **B** ($\Delta T = 92{\cdot}6$°C) over that of **A** ($\Delta T = 83{\cdot}7$°C) was attributed to the greater lateral adhesion of the rod-shaped molecules in **B**, which should be greater the greater the polarity and or the polarizability of the central moiety of the molecule. In **B**, the mutual conjugation between the alkoxy and carbonyl groups increases the polarity of the carbonyl oxygen and so stabilizes the mesophase.

Although the thermogram of each compound in its pure state does not exhibit a solid–solid transition in

Table 2. Transition temperatures (°C) of compounds **A** and **B**.

Compound	Run no.	$S{-}S_1$	$S_1{-}S_2$	S_2–Sm1	Sm1–Sm2	Sm2–I	ΔT
A (ethanol)	First	—	—	133·8	154·5	217·5	83·7
(melt)	Second	—		133·8	154·5	217·5	83·7
B (ethanol)	First	—	109·8	119·8	—	212·4	102·6
(melt)	Second	42·3	103·5	115·5	—	209·0	105·5

S=solid; Sm=smectic; I=isotropic; $\Delta T = T_c - T_m$.

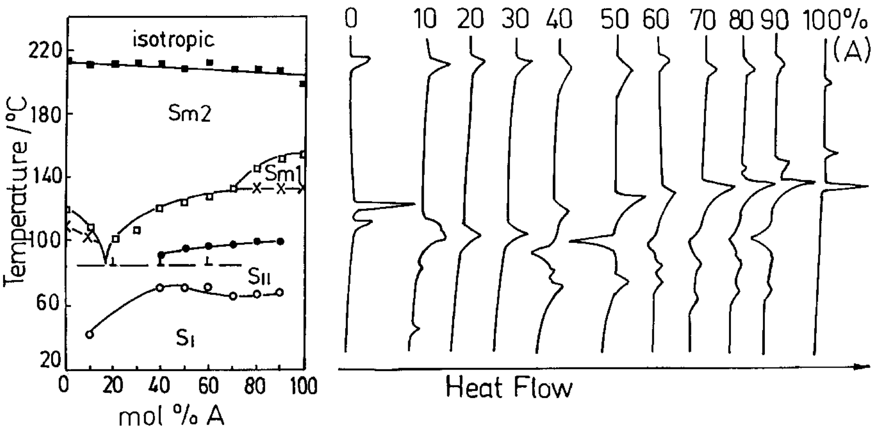


Figure 3. Phase diagram and DSC thermograms for binary mixtures of **A** and **B** (first run).

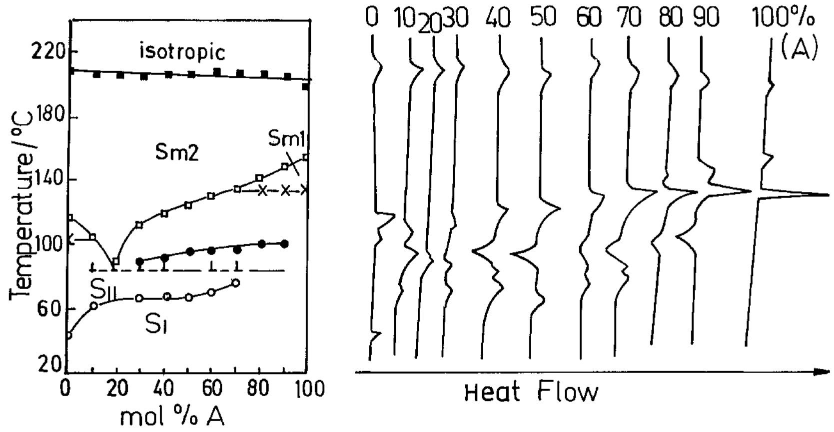


Figure 4. Phase diagram and DSC thermograms for binary mixtures of **A** and **B** (second run).

the neighbourhood of 70°C (for their first run), those of their mixtures (as being prepared from the melt) exhibit a solid–solid endotherm around 70°C, that leads to a metastable solid. The later phase, upon heating, is followed by a crystallization exotherm which, in most cases, overlaps with the eutectic endotherm. On the other hand, their phase diagrams show a linear mesophase–isotropic transition temperature relationship indicating an ideal behaviour in their liquid phases. This behaviour is attributed to similar electronic factors in both compounds since they have, to a first approximation, the same molecular geometry [4, 12]. This indicates, further, that even weak molecular complexes do not form between **A** and **B**, and that the dimers **A**–**A** and **B**–**B** persist in the melt within their mesophases. To investigate whether molecular complexes do exist between molecules of **A** and **B** or not, we tried to examine their molecular interaction, by the polarizability method [20], in an inert solvent to rule out any solute–solvent interactions that may affect complex formation. Unfortunately, both compounds (**A** and **B**) are not soluble in any non-polar solvent, thus the idea was consequently discarded. With regards to their solid-heterogeneous mixtures, a eutectic mixture was obtained at about 15 mol % of **A** that melts at about 84°C and a liquid crystalline range of 122°C.

The first author wishes to thank the German DAAD Foundation who provided the scholarship that enabled him to co-operate with the German scientists and perform this work.

References

[1] Demus, D., Demus, H., and Zaschke, H., 1974, *Flussige Kristalle in Tabellen* (Leipzig).
[2] Dewar, M. J. S., and Schroeder, J. P., 1963, *J. org. Chem.*, **30**, 2296.
[3] Gray, G. W., 1962, *Molecular Structure and Properties of Liquid Crystals* (New York: Academic Press).
[4] Griffin, A. C., and Johnson, J. F., 1977, *J. Am. chem. Soc.*, **99**, 4359.
[5] Sackman, H., and Demus, D., 1963, *Z. Phys. Chem. (Leipzig)*, **224**, 177; ibid., 1965, **230**, 285.

[6] Dave, J. S., Patel, P. R., and Vasnath, K. L., 1966, *Ind. J. Chem.*, **4,** 505.

[7] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. org. Chem.*, **35,** 2711.

[8] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. Am. chem. Soc.*, **92,** 1582.

[9] Steinstrasser, R., 1972, *Angew. Chem.*, **84,** 636.

[10] Steinstrasser, R., 1972, *Z. Naturf. b*, **27,** 774.

[11] Park, W., Bak, C. S., and Labes, M. M., 1976, *J. Am. chem. Soc.*, **97,** 4398.

[12] Griffin, A. C., Fisher, R. F., and Havens, S. J., 1978, *J. Am. chem. Soc.*, **100,** 6329.

[13] Gray, G. W., and Jones, B., 1954, *J. chem. Soc.*, 1467.

[14] Klarmann, E., Gatyas, L. W., and Sternov, V. A., 1932, *J. Am. chem. Soc.*, **54,** 298.

[15] Naoum, M. M., Seliger, H., and Happ, E., 1997, *Liq. Cryst.*, **23,** 403.

[16] Bunning, J. D., and Lydon, J. E., 1979, *J. chem. Soc. Perkin II*, 1621.

[17] Dewar, M. J. S., and Riddle, J., 1975, *J. Am. chem. Soc.*, **97,** 6658.

[18] Elser, W., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 219.

[19] Rao, K. G., and Rao, C. N. R., 1966, *J. mater. Sci.*, **1,** 238.

[20] Naoum, M. M., Saad, G. R., Abdel-Moteleb, M. M., Shinouda, H. G., and Rizk, H. A., 1987, *Can. J. Chem.*, **65,** 2760; ibid., 1989, **67,** 284; ibid., 1990, **68,** 480.