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

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To cite this Article Naoum, Magdi M. , Saad, Gamal R. , Nessim, Refaat I. , Abdel-Aziz, Talal A. and Seliger, H.(1997) 'Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures II. 4-Hexadecyloxyphenyl arylates and aryl 4-hexadecyloxy benzoates', Liquid Crystals, 23: 6, 789 — 795

To link to this Article: DOI: 10.1080/026782997207713
URL: http://dx.doi.org/10.1080/026782997207713

LIQUID CRYSTALS, 1997, VOL. 23, NO. 6, 789–795

Effect of molecular structure on the phase behaviour of some liquid crystalline compounds and their binary mixtures. II. 4-Hexadecyloxyphenyl arylates and aryl 4-hexadecyloxy benzoates†

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(*Received 26 March 1997; accepted 7 July 1997*)

4-Hexadecyloxyphenyl-4′-substituted benzoates, **Ia–d**, and 4-substituted phenyl-4′-hexadecyloxy benzoates, **IIa–d**, with the substituents CH_3O, Cl, CN, and NO_2, respectively, were prepared and characterized by infrared spectroscopy and the apparent solution dipole moment measured using cyclohexane as a solvent. Smectic A mesophase stability was investigated by differential scanning calorimetry and polarized light microscopy. The effects of structural changes on phase transitions in these two series of compounds are discussed in terms of dipole and mesomeric effects.

1. Introduction

Although great effort has been paid to establishing the relative effectiveness of terminal substituents in liquid crystalline compounds for promoting the thermal stability of mesophases, only general trends have been developed [2–5]. Terminal substituents can, of course, both attract and repel one another and they can, in addition, via mesomeric interactions, affect the polarizability of the aromatic ring to which they are attached. Groups which are compact, polar, and/or polarizable, appear to be very effective in creating high clearing points [2]; that is, extending upward the temperature region for the persistence of the mesophase. This has been attributed [2–5] to the increase of intermolecular attraction with increase of polarity, as well as with the polarizability of the substituent. Conversely, as the polarity of the substituent decreases, the clearing points appear to decrease. Hence, in the case of the phenyl benzoate ester system, the mesomorphic phase becomes more persistent when the mesophase stability effect of the mutual conjugation between the *para* substituent and the ester carbonyl group is increased. Thus, while electron-donating substituents expectedly promote the polarity of the carbonyl group, which in turn results in stronger intermolecular attractions, electron-withdrawing substituents which are *para* to the ester oxygen atom reduce the polarity of the carbonyl group, and hence, lower the clearing point of the mesophase [3].

The 4-alkoxyphenyl esters of 4-substituted benzoic acids, **Ia–d**, and their corresponding isomers, 4-substituted phenyl esters of 4-alkoxybenzoic acids, **IIa–d**, seemed to us to be interesting systems for investigating structural effects on mesophase stability. It might be evident that such compounds (as indicated below) possess factors favouring liquid crystallinity, those factors being the geometrical anisotropy manifested by the large molecular length-to-breadth ratio, and the polarity of both end and inner groups [6].

It might be pointed out that these esters were chosen on the basis that in a single series the only difference between its members lies in the electronic nature of the terminal substituent *X*, and that the difference between any two corresponding isomers in the two series is in the location of the ester group, so that such a perturbation in the molecular electronic properties could be a probe to investigate factors bearing on the phase transitions of these compounds.

The alkoxy group chosen was $C_{16}H_{33}O$ because in this type of series [7] a pattern has been seen in which the mesophase–isotropic transition temperature rises with increasing chain length. In the lower homologues

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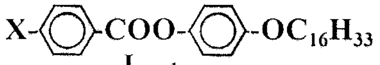
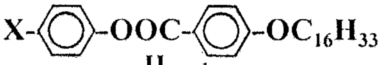
† Part I was published in *Liquid Crystals* [1].


Ia–d


IIa–d

(**a**) X=CH_3O (**b**) X=Cl (**c**) X=CN (**d**) X=NO_2

of a series a nematic mesophase appears, and if the chain length increases there is a tendency for a smectic A phase to appear. Homologues with chain lengths of 16 carbons exhibit only a smectic A mesophase which transforms directly to the isotropic phase [7, 8]. On the other hand, increasing transition temperature with alkoxy group length has been attributed by Gray and Winsor [9] to the fact that lateral attractions grow stronger as the alkoxy group is lengthened while the terminal attractions grow relatively weaker, so that the net result would be a rising mesophase–isotropic curve, levelling off as the series terminates at 16 carbons.

2. Experimental

Chemicals were purchased from the following companies: Aldrich, Wisconsin, USA and E. Merck, Darmstadt, Germany.

2.1. *4-Hexadecyloxybenzoic acid*

This compound was prepared from ethyl-4-hydroxybenzoate and 1-bromohexadecane by the method described in our previous work [10]. The resulting acid was TLC pure and exhibited the following phase transition temperatures: $T_m = 102$°C, $T_c = 131$°C.

2.2. *4-Hexadecyloxybenzoyl chloride*

This was prepared from the acid by heating with excess thionyl chloride under reflux for 5 h. The unused thionyl chloride was removed under vacuum to give the acid chloride as residue.

2.3. *4-Hexadecyloxyphenol*

This compound was prepared from hydroquinone monobenzyl ether and 1-bromohexadecane by the method described before [10]. The product, after crystallization from ethanol, was TLC pure and melted at 83·6°C.

2.4. *4-Hexadecyloxyphenyl-4′-substituted benzoates. (series **Ia–d**)*

This series of compounds was prepared from the corresponding 4-substituted benzoyl chloride and 4-hexadecyloxyphenol by a method described in previous work [10]. One molar equivalent of the acid chloride in dry pyridine was added dropwise to a solution of 4-hexadecyloxyphenol in pyridine over a period of 1 h, and the resulting mixture was heated overnight with stirring at 60°C. The products, crystallized twice from 10% dichloromethane/methanol, were TLC pure; the results of elemental analyses are given in table 1.

2.5. *4-Substituted phenyl-4′-hexadecyloxy benzoates (series **IIa–d**)*

These were prepared in a similar way to series **I** compounds by the reaction of 4-hexadecyloxybenzoyl chloride and the corresponding 4-substituted phenol in pyridine. The products, after being crystallized twice from ethanol, were TLC pure and their elemental analyses are also given in table 1.

2.6. *Physical characterization*

Infrared spectra were measured with a Perkin Elmer B 25 spectrophotometer.

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 J g^{-1} was used

Table 1. Elemental analyses of compounds **Ia–d** and **IIa–d**.

		Elemental analysis: calculated (found)			
Compound	X	% C	% H	% N	% Cl
Ia	CH_2O	76·92 (76·94)	9·40 (9·54)	—	—
Ib	Cl	73·65 (73·65)	8·68 (8·64)	—	7·53 (7·49)
Ic	CN	77·75 (77·83)	8·86 (9·31)		
Id	NO_2	72·05 (72·18)	8·49 (8·42)	2·90 (2·94)	—
IIa	CH_3O	76·92 (76·90)	9·40 (9·44)	—	—
IIb	Cl	73·65 (73·59)	8·68 (8·74)	—	7·53 (7·56)
IIc	CN	Ref [10]			
IId	NO_2	Ref [7]			

for the enthalpy of fusion of indium. Typical heating and cooling rates were 10 K min^{-1}, and sample masses were 1–2 mg.

Transition temperatures were determined with a standard polarized light microscope (C. Zeiss, Germany), attached to a FB 52 hot-stage equipped with a FB 80 central processor (Mettler, Switzerland).

Dipole moments were calculated from measurements of the dielectric constant, density and refractive index for dilute solutions of compounds of both series **I** and **II** in cyclohexane at 30°C [11, 12]. The symbols have the following meaning: ${}_{\mathrm{D}}P_2$ is the molar deformation polarization of the solute obtained by extrapolating the measured molar refraction for the sodium D-line to infinite wavelength [13]; $P_{2\infty}$ is the molar polarization of the solute at infinite dilution taken as the average of that determined graphically and those calculated from the equations of Hedestrand [14], and Palit and Banerjee [15]; μ(D) is the dipole moment determined by the refractivity method from:

$$\mu(\mathrm{D})=0{\cdot}01273(P_{2\infty}-{}_{\mathrm{D}}P_2)^{1/2}.$$

On the basis of precessions of ±0·0005 in dielectric constants, ±0·0001 in refractive indices, and ±0·02% in solution concentrations, the dipole moment values are believed reliable to ±0·05 D.

3. Results & discussion

3.1. *Effect of substituent on dipole moment*

Since the mesophase stability of a liquid crystalline compound is mainly dependent upon the intermolecular interactions, in which molecular polarity plays an important role, it has seemed worthwhile to examine firstly the effect of substituent on the dipole moment of each compound in each of the two series, **Ia–d** and **IIa–d**. Thus, the apparent solution moments of the members of both series were measured at 30°C in cyclohexane as a non-polar solvent using the refractivity method. The results, as calculated by the Hedestrand [14], Palit and Banerjee [15] and graphical methods are summarized in table 2.

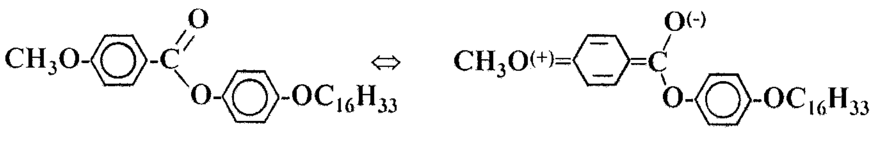
It will be seen from this table that the dipole moment value of any compound is dependent upon the nature of the substituent as well as the location inversion of the ester group within the phenyl benzoate molecule. A change in the extent of conjugation expectedly alters the polarizability of the molecule, and consequently the resultant apparent solution moment.

In the case of methoxy-substituted derivatives, **Ia** and **IIa**, the observed dipole moment values are practically identical, the values obtained being 2·66 and 2·69 D, respectively. This might be accounted for by the fact that the alkoxy groups, CH_3O and $C_{16}H_{33}O$, attached alternatively to the two ends of each of these linear molecules, are practically of the same dipolar character and, in turn, the mesomeric or inner moments resulting from the delocalization of electrons (conjugative interaction) between the oxygen atom of the attached alkoxy groups and the ester C=O group could be practically the same, so that the observed dipole moments appear identical.

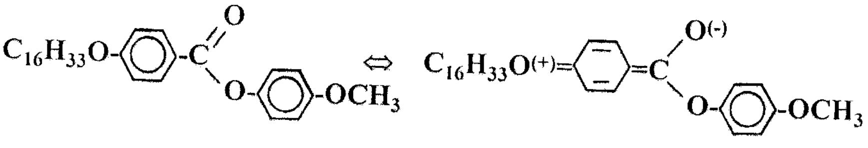
With regard to the chloro-substituted derivatives, **Ib** and **IIb**, the delocalization of electrons between the chlorine atom and ester carbonyl in the former case results in a dipole moment directed opposite to the bond moment of chlorine in the molecule, whereas

Table 2. Polarization data for compounds **Ia–d** and **IIa–d** in cyclohexane at 30°C.

			$P_{2\infty}$/cm^{-3}				
Compound	X	${}_{\mathrm{D}}P_2$ /cm^{-3}	[14]	[15]	Graphical	Average	μ/D
Ia	CH_3O	154·18	298·89	297·60	298·89	298·46	2·66
Ib	Cl	160·01	324·71	323·16	423·70	324·19	2·84
Ic	CN	142·23	448·83	445·56	448·81	447·73	3·87
Id	NO_2	143·08	408·01	405·72	408·01	407·25	3·60
IIa	CH_3O	149·29	297·01	295·54	297·01	296·52	2·69
IIb	Cl	169·84	475·91	472·16	475·90	474·65	3·87
IIc	CN	176·48	875·15	862·64	875·09	870·96	5·84
IId	NO_2	163·39	836·51	819·13	836·41	830·68	5·73



Ia, μ = 2·66 D



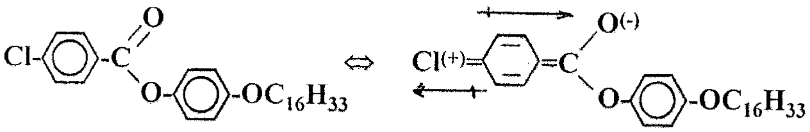
IIa, $\mu = 2{\cdot}69$ D

the delocalization of electrons between the oxygen atom of the alkoxy group $C_{16}H_{33}O$ and the carbonyl group of the ester through the intervening phenylene ring augments the chlorine-bond moment in the other molecule. While in compound **IIb**, such an electronic interaction would, alternatively, occur between the lone pair of the alkoxy oxygen and the ester carbonyl group. This suggestion is born out experimentally by the observation that for **Ib**, the apparent solution moment is 2·84 D, and that for **IIb** is 3·87 D.

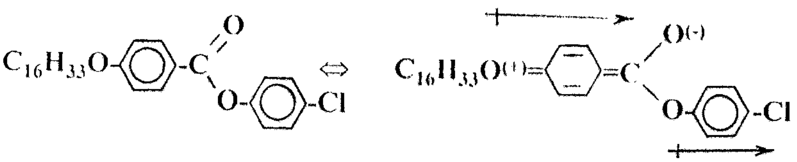
In the case of the cyano- and nitro-substituted derivatives **Ic,d** and **IIc,d** the situation is quite different. If the substituent is in the benzoyl moiety, which is the case for **Ic** and **Id**, there will be opposing conjugative effects on both sides of the molecule. On one side, such competition occurs between the cyano (or nitro group) and the ester carbonyl group, while on the other side, it occurs between the lone pair of the alkoxy oxygen atom and the ester oxygen atom through the intervening phenyl rings. Consequently, it may be inferred that due to these opposite mesomeric effects on each side of the molecules **Ic** and **Id**, there will be no reinforcement of the dipolar character of the compound, in the sense that the observed dipole moment of the molecule mainly originates from group moments situated at the two ends of the molecule. This inference is in harmony with the observation that the apparent solution moments are 3·87 and 3·60 D for compounds **Ic** and **Id**, respectively. In contrast in the corresponding isomers **IIc** and **IId**, the conjugative interactions between the cyano (or nitro) group and the ester oxygen atom on one side of the molecule, as well as that between the alkoxy group ($C_{16}H_{33}O$) oxygen atom and the ester carbonyl group, on the other side, are expectedly unopposed by the other mesomeric effects; at the same time the resulting mesomeric (inner) moments act in the same direction as that of the terminally attached group moments. This again is in harmony with the experimental results; the observed values 5·84 and 5·73 D, respectively, are significantly higher than those of the corresponding isomers in series **I** (table 2).

3.2. *IR absorption spectra*

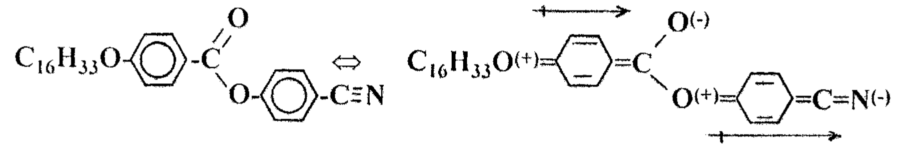
The above conclusions, drawn from dipole moment measurements, can be justified if comparison is made between the infrared absorption spectra of the esters as given in table 3. As expected, the carbonyl groups in compounds **Ia** and **IIa** absorb at practically the same frequency, i.e. at 1730 and 1728 cm^{-1}, respectively, thus supporting the conclusion that the extent of conjugation arising from a CH_3O or $C_{16}H_{33}O$ group at the same end of the molecule is nearly the same. On the other hand, the excess mesomeric interaction in the *p*-chloro derivative **IIb** over its isomer **Ib** is confirmed if comparison is made between $\nu_{C=O}$ for both compounds where their values are 1728 and 1742 cm^{-1}, respectively. The lower value, 1728 cm^{-1}, for **IIb** indicates greater conjugation. Similar conclusions may be arrived at for the nitro-substituted derivatives, **Id** and **IId**, where the carbonyl absorptions occur at 1742 and 1722 cm^{-1}, respectively. That is, mesomerism in **IId** is greater than that in **Id**, as indicated above from dipole measurements. Unexpectedly, the infrared absorption spectra of the



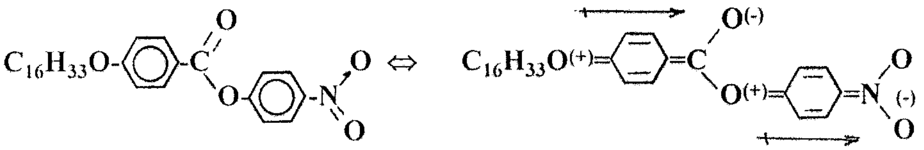
Ib, $\mu = 2{\cdot}84$ D



IIb, $\mu = 3{\cdot}87$ D



IIc, μ = 5·84 D



IId, μ = 5·73 D

Table 3. Characteristic absorption frequencies (cm^{-1}) for compounds **Ia–d** and **IIa–d** in KBr.

X	Compound	$\nu_{C=O}$	$\nu_{C\equiv N}$	Compound	$\nu_{C=O}$	$\nu_{C\equiv N}$
CH_3O	**Ia**	1730		**IIa**	1728	
Cl	**Ib**	1742		**IIb**	1728	
CN	**Ic**	1736	2239	**IIc**	1740	2224
NO_2	**Id**	1742		**IId**	1722	

cyano compounds **Ic** and **IIc** were confusing, since their C=O groups absorb at very close frequencies, i.e. 1736 and 1740 cm^{-1}, respectively. The C≡N absorption frequencies were thus taken instead to evaluate the extent of conjugation. The results, 2239 and 2224 cm^{-1}, observed as the C≡N absorption frequency of **Ic** and **IIc**, respectively, indicate a greater conjugative interaction in **IIc**, and consequently a higher dipole moment value, as inferred above, compared with **Ic**.

3.3. *DSC analysis*

In order to investigate the effect of substituents, and consequently of the dipole moments, on the phase behaviour of the investigated compounds, the DSC analyses for compounds **Ia–d** and **IIa–d** were carried out. The transition temperatures observed are summarized in table 4. The phase transitions were identified by the aid of polarized light microscopy. Differences between temperatures determined by the microscope and those from DSC were within 2–3°C. It is known that significantly strong forces between linear or rod-shaped molecules give rise to an ordered parallel arrangement which would be retained after melting at T_m. That is, if the intermolecular forces (arising from dipole–dipole, dipole–induced-dipole interactions, as well as dispersion forces and hydrogen bonding) are strong enough, linear association of molecules is effected and retained after melting at T_m. At this temperature a liquid crystalline phase is formed since the required parallelism for the anisotropic property of such a compound is satisfied and the obtained mesophase exists over an interval of temperature until the clearance temperature T_c is reached. At this stage, transition from the mesomorphic phase to isotropic liquid takes place. If, however, the intermolecular forces are not sufficiently strong to result in a linear association of molecules, the required parallelism for liquid crystal formation will be disrupted. Conversely, it may happen that the association is so strong that by the time the solid reaches its melting point, T_m, the thermal fluctuation are too intense to permit any preferred substantial order (i.e. parallel alignment of molecules) to remain within the fluid. In this case, the solid passes directly into the isotropic liquid at its melting point, T_m. Based on such reasoning, the results obtained from thermal analyses of the investigated compounds, as shown in table 4, might be tentatively accounted for as explained in the following paragraphs.

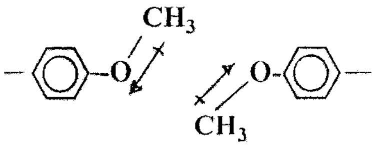
It might be recalled that the dipole moments (2·66 and 2·69 D, respectively) for the methoxy derivatives **Ia** and **IIa** are practically identical, so that the molecular interactions arising on one hand from the dipolar character of these compounds, as well as on the other hand from the lateral interactions between the terminal methoxy dipolar groups of neighbouring molecules, can force these molecules to linear association, with end-to-end organization of the mesophase.

A possible explanation for the phase behaviour of **Ia** and **IIa** may lie in the fact that the forces constituting the meso and crystalline phases are the outcome of two opposing forces, i.e. attractive and repulsive coulombic

Table 4. Transition temperatures (°C) and enthalpy of transitions (kJ mole^{-1}) for compounds **Ia–d** and **IIa–d**.

		On heating					On cooling				
X	Compound	T_m†	ΔH_m	T_c‡	ΔH_c	ΔT	T_m	ΔH_m	T_c	ΔH_c	ΔT
CH_3O	**Ia**	90·9	72·4	—	—	—	(84·1)	73·5	—	—	—
	IIa	96·1	66·9	—	—	—	(63·5)	63·2	(75·0)	2·1	11·5
Cl	**Ib**	103·1	84·0	—	—	—	(95·2)	83·1	—	—	—
	IIb	84·7	62·6	—	—	—	(64·0)	55·8	(73·4)	4·9	9·4
CN	**Ic**	88·2	49·4	106·8	5·9	18·6	(79·1)	48·4	(104·2)	6·5	25·1
	IIc	85·4	61·1	96·3	5·7	10·9	(62·4)	60·6	(90·2)	5·7	27·8
NO_2	**Id**	82·4	60·2	91·7	4·9	9·3	(67·9)	59·8	(90·0)	4·9	22·1
	IId	79·4	54·5	88·7	3·6	9·3	(67·6)	53·9	(87·0)	3·7	19·4

† T_m = solid–smectic A or solid–isotropic transitions.
‡ T_c = smectic A–isotropic transition.



forces [16]. The attractive forces consist primarily of polar carbonyl units along the molecule and terminal dipoles interacting with appropriately charged polar groups of other molecules in the concerned phase. The repulsive forces are mainly determined by interactions between protruding charged ends of the dipole. On the other hand, the effect of the methoxy group in **Ia** and **IIa** seems explicable [17] in terms of a shielding effect on the oxygen lone pairs by an insulator, the methyl group. The repulsive forces involving oxygen lone pairs are thereby substantially reduced, and consequently a decrease in the repulsive forces simply allows a close approach of neighbouring molecules, thus increasing bonding forces. These strong forces will be associated with high melting points and melting enthalpies (table 4) in such a way that no mesophase is detected on heating, as is observed. In these compounds, the melting of crystals occurs at a higher temperature than does the breakdown of the mesomorphic forces; hence there will be insufficient molecular anisotropy to cause the formation of a mesophase on heating. The possible super-cooling effect in the monotropic derivative **IIa** (solidifies at 63·5°C) would allow the persistence of the ordered alignment of molecules and the appearance of a mesophase during cooling. Furthermore in compound **Ia**, the small methyl group attached to the benzoyl moiety furnishes poor insulation against terminal repulsion between similar ends of the dipoles. As the size of the alkyl group increases to $C_{16}H_{33}$ in **IIa**, these repulsion forces decrease and the lateral intermolecular attractions increase. Thus compound **IIa** is expected to be of a higher melting point than **Ia**, as observed from table 4.

In the case of the cyano (**Ic** and **IIc**) and nitro (**Id** and **IId**) derivatives one might expect that in view of the highly dipolar terminal CN and NO_2 groups, the dipole–dipole interactions together with their mesomeric effects (particularly if substitution is in the phenolic residue of the molecule as in **IIc** and **IId**) would favour liquid crystal formation. This is born out experimentally, as given in table 4, in which these derivatives appear to be enantiotropic. It might be noted that although the dipole moments of compounds **IIc** ($\mu = 5{\cdot}84$ D) and **IId** ($\mu = 5{\cdot}73$ D) are greater than those of their corresponding isomers **Ic** ($\mu = 3{\cdot}87$ D) and **Id** ($\mu = 3{\cdot}60$ D), respectively; their crystal–mesophase, T_m, as well as their mesophase–isotropic, T_c, transition temperatures behave in an opposite manner. This may again be explained in terms of repulsive forces. In the case of the cyano (**IIc**) and nitro (**IId**) compounds, the repulsive contribution predominates and thereby lowers both T_m and T_c, compared with their corresponding isomers **Ic** and **Id**.

Similarly, an explanation could be made for the phase behaviour of the chloro derivatives **Ib** ($\mu = 2{\cdot}84$ D) and **IIb** ($\mu = 3{\cdot}87$ D). As pointed out above, the extent of conjugation in **IIb** is greater than in **Ib**, thus the repulsive force between the charged ends of the molecule **IIb** is more pronounced, and consequently a lower melting point is observed for **IIb** ($T_m = 84{\cdot}7$°C) than for **Ib** ($T_m = 103{\cdot}1$°C). In both cases, association of molecules is so strong (as evidenced from their high enthalpies of melting, ΔH_m) that at their melting points no mesophase is detected on heating. On the other hand, on cooling, strong intermolecular attractions in **Ib** ($\Delta H_m = 83{\cdot}1$ kJ mol^{-1}) prevent the appearance of a mesophase and a solid is formed directly at 95·2°C. On the contrary, the relatively weaker intermolecular forces in **IIb** ($\Delta H_m = 62{\cdot}6$ kJ mol^{-1}) allow the formation of the mesophase on cooling at 73·4°C before it solidifies at 64·0°C.

It can also be seen from table 4 that in the case of the two monotropic derivatives **IIa** and **IIb**, the enthalpy of solid–isotropic transition during heating (ΔH_m) approximately equals the sum of those due to isotropic–mesophase (ΔH_c) and mesophase–solid (ΔH_m) transitions, during cooling. This provides extra evidence that greater energy is required to rupture the molecular associations in the solid phase to form an isotropic liquid compared with that required to transfer it to the anisotropic liquid; the difference is that required to destroy molecular ordering in the mesophase. Additionally, those derivatives possessing no mesophase at all (**Ia** and **Ib**) have higher ΔH_m values than those of the corresponding monotropic derivatives.

In conclusion, one may suggest that, in view of the various factors governing the tendency of a compound to exhibit liquid crystallinity, a rough measure of this tendency is the length of the temperature over which the anisotropic parallelism of linear association is retained before being converted into the isotropic liquid phase. That is, the difference ΔT ($=T_c - T_m$) is a rough measure of the capacity of a compound for liquid crystalline formation. Accordingly, table 4 signifies that this tendency for the compounds investigated decreases in the following order:

IIc > **Ic** > **Id** > **IId** > **IIa** > **IIb**.

The first author would like to thank the German DAAD foundation for offering the scholarship that enables him to prepare the compounds investigated in the laboratory of Prof. Seliger.

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