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Preliminary communication

The effect of a substituent in the central ring on the liquid crystalline properties of di(4-alkoxycarbonylphenyl) terephthalates

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Four series of di(4-alkoxycarbonylphenyl) terephthalates with different lateral substituents in the central ring and lengths of the terminal alkyl groups were synthesized. The influence of the lateral substituent on thermodynamical parameters of the phase transitions and elastic properties of the nematic phases (ratio of bend elastic constant to diamagnetic anisotropy $K_3/\Delta\chi$) were studied by polarizing optical microscopy, differential scanning calorimetry and observations of the Fréedericksz transition. It was found that increasing the alkyl chain length and the substituent size in the sequence H, Cl, Br, NO_2 results in reduction in stability of the crystal and (as frequently observed in other cases) the liquid crystal phases. The changes in the bend elastic constant and the melting enthalpy caused by the substituent variation are correlated with each other, a fact that is explained by the dependence of short-range lamellar packing on size and polarity of substituent.

It is well known that introducing a lateral substituent into an aromatic ring of a liquid crystalline compound usually lowers the melting temperature and thermal stability of both smectic and nematic mesophases [1]. The effects of lateral substitution on the thermodynamic parameters for the N → I (nematic → isotropic) transition of 2-substituted 1,4-phenylene di-*p*-anisates have been investigated by Dewar and co-workers [2, 3]. They found that the N → I transition temperature decreases, but that the transition enthalpy and entropy increase with increasing size of the halogen substituent used in the central ring. The observations were explained by the authors in terms of interlocking of the substituents on different molecules and decreasing of the mean intermolecular distance.

Another class of LC compounds is the di(4-alkoxycarbonylphenyl) terephthalates (ACPT) for which the influence of the length of the terminal alkyl groups on the thermodynamic parameters of the phase transitions have been investigated [4]. The ACPT structure has also been used as mesogenic unit in constructing polymer chains containing aromatic triads alternating with flexible spacers [4, 5]. Except for the dimethyl, diethyl and dipropyl compounds which have nematic phases, other homologous ACPT, with longer alkyl groups form only smectic phases. According to this work the LC → I transition enthalpy increases with increasing length of terminal alkyl group.

The present paper deals with the synthesis and investigation of the liquid crystalline properties of the di(4-alkoxycarbonylphenyl) terephthalates with different substituents in the central phenylene ring. Our aim was to study the influence of the substituents on the mesomorphic properties and the nematic bend elasticity of the compounds.

2-Chloro- and 2-bromo-terephthaloyl dichlorides were obtained according to the procedure described in [6] by halogenation of *p*-xylene in the presence of Fe, followed by oxidation of the 2-chloro- and 2-bromo-*p*-xylenes by oxygen, using $Co(Ac)_2$ as a catalyst, into the

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corresponding terephthalic acids, which were then heated with $SOCl_2$ in the presence of DMF. The products were distilled in vacuum. Yields: 7·4 g (60%) of 2-chloroterephthaloyl dichloride, b.p. 150–153°C/15 mm (144°C/10 mm [6]); 25 g (86%) of 2-bromoterephthaloyl dichloride, b.p. 168–170°C/22 mm (158°C/11 mm [6]).

4,4′-(2-Bromoterephthaloyldioxy)dibenzoyl dichloride was synthesized according to a previously described procedure [7] from 31·2 g (0·2 mol) of 4-hydroxybenzoic acid dissolved in 380 ml of 2·1*M* NaOH and 25 g (0·088 mol) of 2-bromoterephthaloyl dichloride dissolved in 175 ml of CCl_4 by stirring together for 2 h. The white precipitate was filtered off, washed and dried. Then, it was heated at reflux with 25 ml of $SOCl_2$ in the presence of DMF. The product was filtered off, twice crystallized from toluene and chloroform, and dried in vacuum. Yield: 10 g (61%), m.p. 195°C (186–188°C [7]). Elemental analysis: calc. for $C_{22}H_{11}BrCl_2O_6$: C 50·61, H 2·32; found: C 50·62, H 2·41%.

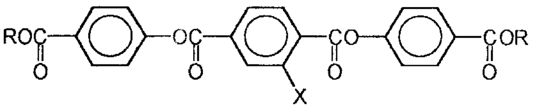
4,4′-(2-Chloroterephthaloyldioxy)dibenzoyl dichloride was obtained and purified by the same procedure. Yield: 5·8 g (59%). Elemental analysis: calc. for $C_{22}H_{11}Cl_3O_6$: C 55·32, H 2·32; found: C 55·31, H 2·40%.

Di(4-ethoxycarbonylphenyl) 2-chloroterephthalate was obtained by heating 0·3 g (0·63 mmol) of 4,4′-(2-chloroterephthaloyldioxy)dibenzoyl dichloride at reflux in a mixture of 5 ml of absolute ethanol and 5 ml of diphenyl ether for 4 h, while bubbling dry argon through the suspension. The excess of alcohol was distilled off and the mixture poured into 50 ml of octane. The precipitate was filtered off and recrystallized from a mixture of toluene/octane, 1 : 1 (vol). Yield: 0·210 g (67%).

All other esters of the structure shown in table 1 were synthesized according to the same procedure in yields of 50–70%. The synthesis of the nitro substituted analogues was described previously [8], and analytical data are given in table 2 for the series **1**, **2** and **3**.

The determination of melting points and transition

Table 1. Thermotropic transition temperatures, transition enthalpies and transition entropies (lower lines) of the di(4-alkoxycarbonylphenyl) terephthalates.



Compound	*X*	*R*	Phase transition/°C (DSC)	Transition enthalpy/kJ mol^{-1} Transition entropy/J mol^{-1}
1a	H	Me	Cr 235 N 324 I	Cr 55·2 N 108·7
1b	H	Et	Cr 189 Sm 205 N 244 I	Cr 41·2 Sm 89·2
1c	H	Pr	Cr 125 Sm 208 N 226 I	Cr 38·1 Sm; N 4·2 I 96 8·4
1d	H	Bu	Cr 141 Sm 194 N 226 I	Cr 40·1 Sm 4·1 I 96·7 8·8
2a	Cl	Me	Cr 186 N 242 I	Cr 41·4 N 0·61 I 90·2 1·18
2b	Cl	Et	Cr 139 N 162 I	Cr 38·8 N 0·35 I 94·2 0·80
2c	Cl	Pr	Cr 86 Sm 105 N 141 I	Cr 29·0 Sm 0·31 N 0·16 I 80·7 0·83 0·38
2d	Cl	Bu	Cr 93 Sm 99 I	Cr 26·3 Sm 1·99 I 71·9 5·35
3a[a]	Br	Me	Cr 178 N 225 I	
3b	Br	Et	Cr 142 I Cr (130 N) 143 I	Cr 45·3 I (N 0·39 I) 109·2 0·94
3c	Br	Pr	Cr 91 N 114·8 I	Cr 34·1 N 0·096 I 94 0·25
3d	Br	Bu	Cr 93 I	Cr 36·9 I 100·9
4a[a]	NO_2	Me	Cr (216 Sm) 218 N 230 I	
4c[a]	NO_2	Pr	Cr (94 Sm) 95 N 124 I	

[a] Results from polarizing optical microscopy.

Table 2. Elemental analysis data for the synthesized esters **1**–**3** (see table 1).

	Calculated/%		Found/%	
Compound	C	H	C	H
1a	66·44	4·29	66·53	4·30
1b	67·67	4·80	67·45	4·73
1c	69·49	5·69	69·32	5·66
1d	68·56	5·34	68·67	6·03
2a	61·48	3·65	61·39	3·73
2b	62·85	4·26	62·66	4·53
2c	64·06	4·80	63·89	4·97
2d	65·16	5·26	65·03	5·50
3a	56·16	3·34	56·23	3·41
3b	57·69	3·91	57·62	4·00
3c	59·06	4·42	59·12	4·51
3d	60·31	4·89	60·22	4·90

temperatures, as well as polarizing-optical observations, were carried out using a Boetius apparatus (GDR, VEB Analytik). Calorimetric determinations were made with a Mettler TA-4000 DSC-20 calorimeter. The ratio of the bend elastic constant to the diamagnetic anisotropy $K_3/\Delta\chi$ of the nematic phase was obtained by the Fréedericksz transition method in a magnetic field. The Fréedericksz transition in a homeotropic layer between a flat and a spherical surface of quartz glass was registered by the optical method [9]. The critical thickness z_c of a layer in a magnetic field **H**

$$z_c = \frac{\pi}{\mathbf{H}}\left(\frac{K_3}{\Delta\chi}\right)^{1/2}$$

was calculated by the formula

$$z_c = R - \left(R^2 - \frac{d^2}{4}\right)^{1/2}$$

where R is the radius of the spherical surface ($R = 4\,\text{cm}$) and d is the measured diameter of the central homeotropic region of the layer undeformed by the magnetic field. The $K_3/\Delta\chi$ value was determined from the slope of the linear dependence of z_c on $1/\mathbf{H}$. Examples of experimental dependencies are presented in figure 1.

One can see in table 1 that the thermodynamical parameters of the phase transitions are influenced by both the nature of the lateral substituent and the length of the alkyl groups. In all the series of esters an increase in length of the terminal groups generally leads to a depression of both the melting and clearing temperatures. The same effect on the phase transition temperature is produced, as would be expected, by the increase in size of the lateral substituent. The temperature range of the mesophase existence ΔT shows an odd–even effect: the dimethyl and dipropyl esters have wider ranges than the others; this effect is most pronounced in series **3** (with the largest substituent in the series).

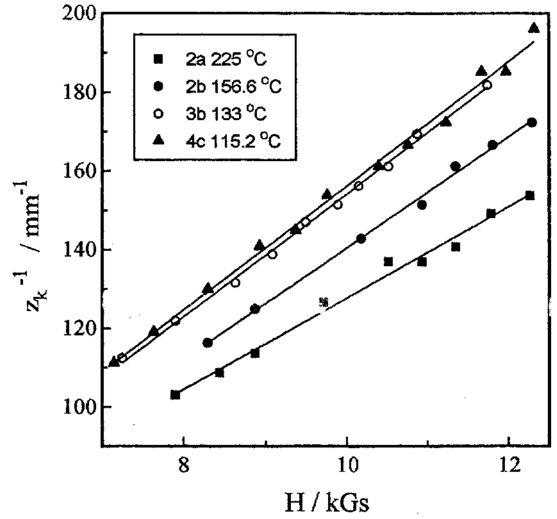


Figure 1. Plot of reciprocal critical thickness Z_k^{-1} of a homeotropic nematic layer versus the magnetic induction **H** for some compounds at the reduced absolute temperatures ($T/T_{NI} = 0{\cdot}98$) shown.

The influence of the structural changes on the transition enthalpies and entropies is diverse in nature. The N–I transition enthalpy decreases in all series with increase in the length of the terminal alkyl groups and the size of the substituent. The behaviour of the melting enthalpy on average is the same in each series, but its value in series **2** is less than in series **1** and **3**.

The dependencies of $K_3/\Delta\chi$ as a function of reduced absolute temperature T/T_{NI} are presented in figure 2. The temperature variation of $K_3/\Delta\chi$ for esters **1c**, **2c**, **4a** and **4c** shows pretransitional effects increasing near the nematic–smectic transition due to strong smectic order fluctuations. As the diamagnetic anisotropy $\Delta\chi$ of liquid crystals depends mainly on the number of aromatic rings, a comparison of the value of $K_3/\Delta\chi$ for the different compounds can be made on the assumption that $\Delta\chi$ is the same for all series. The temperature behaviour of $K_3/\Delta\chi$ is governed by variation in the order parameters. Due to the small nematic ranges and the influence of smectic order parameter fluctuations on the value of $K_3/\Delta\chi$, the comparison is presented for some of the compounds at the reduced temperature $T/T_{NI} = 0{\cdot}98$ (figure 3). One can easily see that the presence of lateral substituents appreciably influences $K_3/\Delta\chi$. It is obvious that the Cl substituted esters **2** have the greatest values of $K_3/\Delta\chi$. The $K_3/\Delta\chi$ value of the unsubstituted esters **1** and the Br substituted esters **3** are practically the same. The $K_3/\Delta\chi$ value of the NO_2 substituted esters **4** occupies an intermediate position. Increasing the aliphatic chain length leads to a decrease of the bend elastic constant in all series.

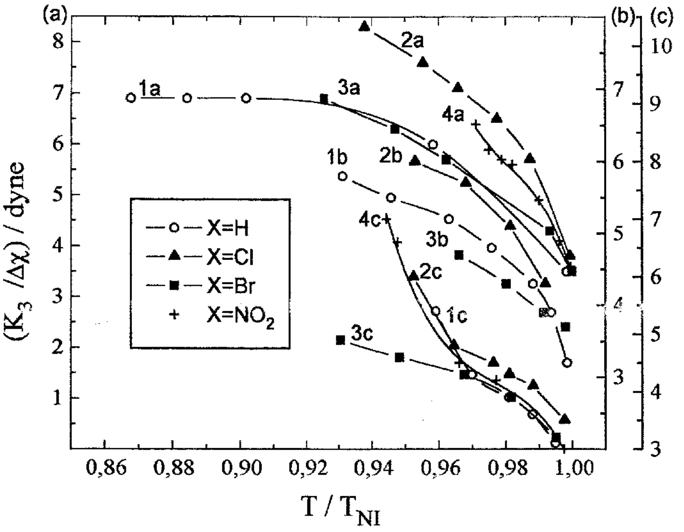


Figure 2. Ratio of bend elastic constant to diamagnetic anisotropy $K_3/\Delta\chi$ for the nematic phases of the compounds studied as a function of reduced absolute temperature T/T_{NI}. Note the different scales for compounds **b** and **c**.

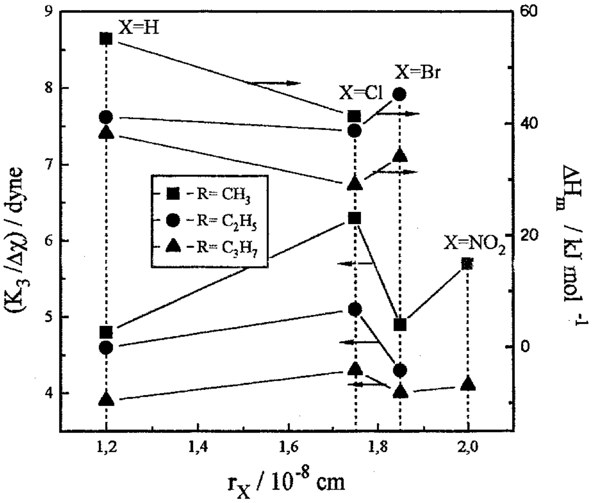


Figure 3. Ratio of bend elastic constant to diamagnetic anisotropy $K_3/\Delta\chi$ for the nematic phases at a reduced absolute temperature $T/T_{NI} = 0{\cdot}98$ versus the size of substituent r_x; see the lower sets of data points arrowed to scale on the left. Top set of data points (arrowed to right) relate to the enthalpy (ΔH) as a function of substituent size r_x, again at a reduced temperature $T/T_{NI} = 0{\cdot}98$.

The results obtained show that the length of alkyl groups and the substituent size determine the type of mesophase formed. Longer molecules form more ordered mesophases, and the axial ratio of the molecules of the unsubstituted esters **1** ($L/d > 3{\cdot}5$) is most favourable for the formation of such mesophases. Actually, three of these esters have a smectic phase. The size of bromine is so large that none of the esters **3** was able to form a smectic mesophase, and ester **3d** was not even liquid crystalline. The chlorine substituted esters occupy an intermediate position: two of them (**2c** and **2d**) have only a smectic phase.

An increase of the volume of X leads to an increase in the distances between molecules in the direction normal to their long axes and as a result to a decrease in the lateral interactions. The uniform influence of the lateral substituents on the thermodynamic properties and elastic bend constant can be seen obviously from figure 3. For Cl substituted esters **2**, the melting enthalpy is lower and the elastic bend constant higher than those for the other series.

It is well known that properties of the nematic phase depend on long-range orientational order as well as short-range positional order. A lamellar packing of molecules is disrupted by increased substituent size, but enhanced by increased polarity of the substituent. The Cl, Br and NO_2 substituents, which have a greater size than H, disrupt long-range and short-range positional smectic order. However, due to the smaller size and the similar polarity of Cl and the larger size and greater polarity of NO_2 (in comparison with Br), the nematic phases of the compounds in series **2** and **4** involve more ordered short-range lamellar packing. This ordering leads to an increase in the short-range correlation in a plane perpendicular to the director, and to an increase in the value of the bend elastic constant K_3. This reasoning allows us to explain the lower value of the melting enthalpy of the Cl substituted compounds on the assumption that the enthalpy values of the solid states of all the compounds are nearly the same.

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