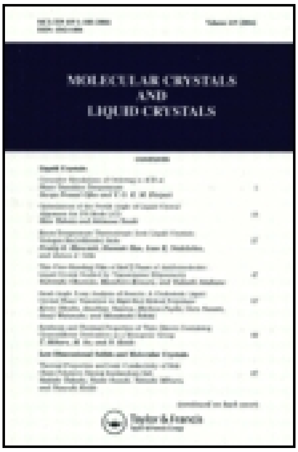

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Effect of Terminal Substituents on the Molecular Dipole Moments of Liquid Crystalline 4-(Trans-4′-n-Alkylcyclohexyl) Benzoates

Z. Raszewski [a], J. Rutkowska [a], J. Kedzierski [a], J. Zielinski [a], J. Zmija [a] & R. Dabrowski [a]

[a] Institute of Technical Physics WAT, 00-908, Warsaw, Poland

To cite this article: Z. Raszewski, J. Rutkowska, J. Kedzierski, J. Zielinski, J. Zmija & R. Dabrowski (1992): The Effect of Terminal Substituents on the Molecular Dipole Moments of Liquid Crystalline 4-(Trans-4′-n-Alkylcyclohexyl) Benzoates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 215:1, 349-356

To link to this article: http://dx.doi.org/10.1080/10587259208038543

Mol. Cryst. Liq. Cryst. 1992, Vol. 215, pp. 349–356
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Printed in the United States of America

THE EFFECT OF TERMINAL SUBSTITUENTS ON THE MOLECULAR DIPOLE MOMENTS OF LIQUID CRYSTALLINE 4-(TRANS-4'-n-ALKYLCYCLOHEXYL) BENZOATES

Z.RASZEWSKI,J.RUTKOWSKA,J.KEDZIERSKI,J.ZIELINSKI,J.ZMIJA,
R.DABROWSKI
Institute of Technical Physics WAT, 00-908 Warsaw, Poland

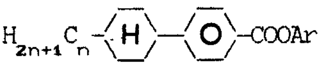
(*Received March 14, 1991*)

Abstract The dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) of aryl 4-(trans-4'-n-alkylcyclohexyl)benzoates have been determined The influence of the substituents on the dipole moment of the investigated esters has been discussed.

Keywords: nematics, dipolemoments, dielectric constants

INTRODUCTION

In[1-2] the synthesis and the temperatures and enthalpies of the phase transitions and some dielectric constants for four series of esters of the general formula:

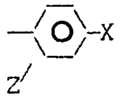


were described.

The aryl (Ar) substituents were as follows:

Series I : n=5, Ar = α-, β- or γ- pyridyl,

Series II - IV : Ar =



where:

Series II : n=5, Z=H, X=H,F,Cl,Br,J,CHO,$CH(OCH_3)_2$, $COCH_3$,CN,NO_2, $N(CH_3)_2$,NCS,SCN,OH,$OCOCH_3$,CH_2CN,CH_2CH_2CN, CH_3,C_2H_5,C_4H_9,C_5H_{11},C_6H_5,OCH_3,OC_8H_{17};

Series III: n=2÷10, Z=H, X=CN,NO_2;

Series IV : n=2÷10, Z=CN, X=C_4H_9,C_5H_{11}.

The wide range of nematic phase of 4-(trans-4'-n-alkylcyclohexyl) benzoates facilitates the dielectric measurements and makes easy the observation of changes of dielectric characteristics due to change of the position of the substituent or introduction of a new one. To learn about the influence of terminal substituents on the molecular dipole moments the 22 chosen esters were investigated by means of dielectric measurements.

RESULTS

In Table 1 the results of the dielectric measurements of 4-(trans-4'-n-alkycyclohexyl) benzoates are summarized for some temperatures T at chosen distances $T-T_c$ from clearing points T_c. The measuring set up and the cell construction are described in[3].

All of the thermal characteristics for the perpendicular $\varepsilon_\perp$ and parallel $\varepsilon_\parallel$ components of the electric permittivities for the investigated esters may be classified into two groups. To the first group belong dielectric characteristics of esters which have only nematic phase (esters from 1 to 16). To the second group belong dielectric characteristics of esters which have both nematic phase and some smectic phases. In this group one can find characteristics for the ester 17 with S_E phase, ester 18 with S_A phase and those from 19 to 22 with both S_A and S_B phases.

DISCUSSION

The values of the principal components of the permittivity tensor $\varepsilon_\parallel$ and $\varepsilon_\perp$ measured for nematic phase and presented in Table 1, were the base for estimations of the effective values of the components $p_\parallel$ and $p_\perp$ of the molecular dipole moments of same investigated esters. To do it the well known Maier and Meier equations[4-5] were used.

$$p_\parallel^2 = \left[\left(\frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\right)^{-1}\frac{\Phi}{\bar{\varepsilon}}\left(\bar{\varepsilon}-1-\frac{2\Delta\varepsilon}{3S}\right)-\alpha_L\right]kT\Phi \qquad (1)$$

$$p_\perp^2 = \left[\left(\frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\right)^{-1}\frac{\Phi}{\bar{\varepsilon}}\left(\bar{\varepsilon}-1-\frac{\Delta\varepsilon}{3S}\right)-\alpha_t\right]kT\Phi \qquad (2)$$

where: $\Phi = 1 - \frac{3N}{\varepsilon_o(2\bar{\varepsilon}+1)}\,\frac{2\bar{\alpha}(\bar{\varepsilon}-1)}{9}$, $\Delta\varepsilon=\varepsilon_\parallel-\varepsilon_\perp$, $\bar{\varepsilon} = \frac{\varepsilon_\parallel+2\varepsilon_\perp}{3}$, $\bar{\alpha} = \frac{\alpha_\parallel+2\alpha_\perp}{3}$

TABLE 1 Dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for chosen esters, their calculated dipole moments $p_{\parallel}$ and $p_{\perp}$ and dipole moments $p_{\parallel Ar}$ and $p_{\perp Ar}$ of the Ar substituent groups. All of the values of dipole moments are given in Debye units.1D = 3.33 10^{-30} Cm.

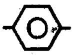
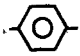
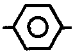
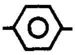
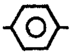
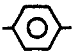
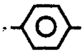
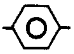
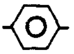
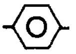
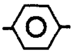
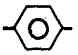
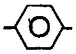
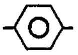
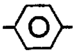
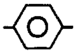
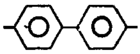
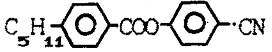
No	-Ar	T_c K	$T-T_c$ K	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$p_{\parallel}$	$p_{\perp}$	$p_{\parallel Ar}$	$p_{\perp Ar}$
1		381	-10	30.00	15.60	5.3	3.4	2.2	0
2	-C_5H_{11}	396	-10	3.81	4.75	-0.6	2.7	-2.4	3.5
			-30	3.76	5.04				
			-50	3.70	5.38				
3	-H	387	-10	3.87	3.21	1.2	1.1	0	0
			-30	4.44	3.52				
4	-F	429	-10	6.65	4.05	2.7	1.4	1.47	0
			-30	8.00	4.10				
			-50	9.25	4.45				
			-70	10.50	4.85				
5	-Cl	464	-10	6.05	3.55	2.9	1.1	1.59	0
			-30	7.35	3.60				
			-50	8.60	3.90				
			-70	9.90	4.20				
6	-Br	466	-10	5.10	3.55	2.8	1.5	1.57	0
			-30	6.20	3.40				
			-50	7.25	3.55				
			-70	8.25	3.75				
7	-J	459	-10	4.90	3.25	3.0	1.6	1.40	0
8	-CHO	474	-10	9.5	5.3	3.9	2.3	2.45	1.7
			-30	11.8	5.8				
			-50	14.4	6.4				
			-70	16.8	7.3				
9	-CN	499	-30	13.7	5.8	4.7	1.7	4.05	0
			-50	19.6	6.8				
			-70	24.4	7.5				
10	-CH_2CH_2CN	458	-10	11.0	6.8	3.6	2.8	4.05	0
			-30	12.3	7.1				
			-50	12.8	7.3				

TABLE 1 (continued)

No	-Ar	T_c K	$T-T_c$ K	$\varepsilon_\parallel$	$\varepsilon_\perp$	$p_\parallel$	$p_\perp$	$p_{\parallel Ar}$	$p_{\perp Ar}$
11	-NO_2	474	-10	14.6	6.1	5.3	1.5	4.01	0
			-30	19.5	6.5				
			-50	24.0	7.0				
			-70	26.2	7.1				
12	-SCN	508	-30	6.7	3.3	3.5	2.1	2.16	2.7
			-50	8.3	3.6				
			-70	9.3	3.8				
13	-CH_3	449	-10	3.46	3.06	1.2	1.4	-0.37	0
			-30	3.65	3.13				
			-50	3.90	3.32				
			-70	4.00	3.40				
14	-$COCH_3$	482	-10	14.3	8.9	4.1	2.8	1.98	2.2
			-30	19.5	10.0				
15	-OH	491	-30	4.9	4.5	1.7	2.3	0	1.5
16	-OCH_3	485	-30	3.7	3.4	1.3	1.8	-0.40	1.2
			-50	3.9	3.6				
17	-CH_2CN	438	-10	9.2	4.4	3.9	3.4	1.35	3.8
			-30	9.6	5.4				
18	-NCS	508	-30	6.7	3.3	3.6	1.0	3.6	0
			-50	8.3	3.6				
			-70	9.3	3.8				
19	-OC_8H_{17}	451	-10	2.92	2.74	0.9	1.1	-0.40	1.2
20	-C_4H_9	431	-10	3.30	3.23	1.1	1.9	-0.37	0
21	-C_5H_{11}	445.5	-10	3.18	2.98	1.0	1.4	-0.37	0
22		540	-50	3.6	2.8	1.4	1.1	0	0
			-70	4.0	3.0				

Here N is the number of molecules in 1 m^3 of liquid crystal characterized by molecular order parameter S(T). α_L and α_t are the longitudinal and the transversal polarizability of the molecule.

Since we had not experimental results for densities and refractive indices n_o and n_e of the investigated esters we had to assume that:

i) the densities $\varrho(T)$ of investigated nematics are just the same as the density of  (5BCP)[6] , obviously extrapolated to the proper temperature range T,

i)the degrees of orientational ordering of all nematics are described by the same theoretical order parameter $S(\tau)$[7], where $\tau=(T-T_c)/T_c$.

The α_L and α_t of investigated substances were obtained by adding to the values of α_L and α_t for 5BCP[8] proper corrections for chemical constitution and molecular structure. The corrections were calculated on the basis of the bond-polarizability derived from the model of polarizability tensor additivity. All data, needed for calculations were taken from[9].

As estimated, the accuracies of determinations of S, ϱ, α_L, α_t are comparable with the accuracies of measurements of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$. The results of the calculations of $p_{\perp}$ and $p_{\parallel}$ for the chosen esters and the perpendicular $p_{\perp Ar}$ and parallel $p_{\parallel Ar}$ components of the dipole moment of the -Ar substituent group for each ester are summarized in Table 1.

To learn about the influence of the $p_{\parallel Ar}$ of substituents on the $p_{\parallel}$ of esters, the obtained results were put on the Figure 1 in the form of points with coordinates $(p_{\parallel Ar}, p_{\parallel})$.
As it is seen in Fig.1 there is a linear correlation between $P_{\parallel}$ and $p_{\parallel Ar}$:

$$p_{\parallel} = 1.41D + 0.91p_{\parallel Ar}$$

According to this equation the value of 1.41D should be the value of $p_{\parallel}$ for (pentylcyclohexyl)benzoate group. It is only about 10 per cent higher than the value of $p_{\parallel}$=1.28D obtained by adding $p_{\parallel}$ of the pentyl benzoate group[10] and $p_{\parallel}$ of the methyl benzene compound[11]. Taking the above and the fact that the slope of the line from Fig.1 is a little smaller than 1 one can state that in case of the investigated compounds the substituent -Ar group gives additive contributions to the total molecular dipole moment. It is not understood for strongly polar groups such as substituents with -CN and $-NO_2$ (ester 9 and 11). Former investigations for different kinds of cyanomesogens[12-13] indicated that the antiparallel associations occur in all those cases. This process is responsible for the fact that the effective dipole moments (calculated from equations 1 and 2), particulary the parallel components are much lower that those for the isolated molecules. Though estimation of dipole moments is approximate it seems that linear correlation between $p_{\parallel}$ and $p_{\parallel Ar}$ is not the result of errors. May be high temperature where nematic phase appears, destroys antiparallel correlations of dipole moments.

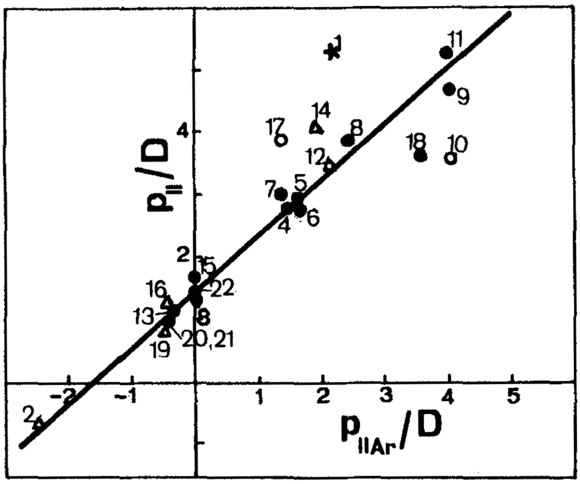


FIGURE 1 Correlation between $p_{\parallel}$ and $p_{\parallel Ar}$ for chosen esters. Details can be found in the text.

The conclusions about intramolecular charge transfer in ester 1 with a α-pyridyl ring[1] are also supported by our investigations. If this transfer appears in this compound, its molecule should be a dipole with a long arm. It would tend to favor intermolecular electrostatic interactions, which would lead to antiparallel arrangement of neighbouring molecules. Because this kind of interactions is responsible for formation of bimolecular smectic layers[14], these molecules would be ideal objects for forming such structures. High value of $p_{\parallel}$ for ester 1 characterized by rather low clearing temperature and some microscopic observations lead to a suggestion[15] about nonelectrostatic origin of bimolecular layers.

Since there are some difficulties with accurate determination of $p_{\parallel Ar}$ for esters 17 and 10, their positions in Fig.1 are rather arbitrary.Moreover,there are any physical reasons to interpretate deviations from linearity for esters 14 and 18 respectively.

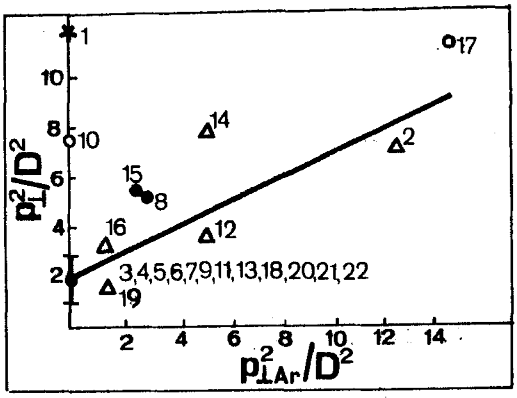


FIGURE 2 Correlation between $p^2_{\perp}$ and p^2_{Ar} for chosen esters. Details can be found in text.

A contribution of perpendicular component of dipole moment of a substituent $p_{\perp Ar}$ to the analog component of all molecule strongly depends on a mutual relative orientation.

Assuming that all rotations of all polar parts of a molecule are free, the following equation may be written[10]:

$$p^2_{\perp} = \Sigma p^2_{\perp Ar}$$

where $p_{\perp i}$ is a perpendicular component of dipole moment of i-th part of a molecule.

To learn about the correlation of the above suggestions Fig.2 was plotted in the form of points with coordinates ($p^2_\perp$,$p^2_{\perp Ar}$)
The mean value from all molecules with $p_{\perp Ar}$=0 is marked in Fig.2 by full circle together with its dispersion. The other esters are marked the same as in case of Fig.1.

We can see that the obtained linear correlation between $p^2_\perp$ and $p^2_{\perp Ar}$ is considerably worse than it was in Fig.1. Generally, a vectc of $p_{\perp Ar}$ prefers antiparallel orientation to vector of p .

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