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Effect of dipole moment and conformation on the mesophase behavior of di-laterally substituted phenylazophenyl benzoate liquid crystals

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ABSTRACT

The dipole moments of the previously prepared 4-(3′-fluoro phenylazo)-2-(or 3-) substituted phenyl-4′′-alkoxybenzoates (**I***n*$_{a-d}$), have been determined in benzene at 30 °C. The data obtained were compared with those theoretically calculated by molecular modeling program to deduce the most probable conformations for each individual homologous series. Probable conformations deduced were found to vary according to type and position of the lateral substituent attached to the central benzene ring. The results were used to correlate the mesophase behavior, in pure and mixed derivatives, with the conformation deduced for each series. Each homologous series, that have in common a lateral fluorine atom on the first terminal ring, differs from the other by a second lateral group substituted on the central ring. The latter group varies between 2-CH_3, 3-CH_3, 2-Cl and 3-CN groups. Within each homologous series, the number of carbons in the other terminal alkoxy group varies between 8 and 16 carbons. The study aims to investigate the steric effect of the spatial orientation of the central lateral substituent, based on deduced conformations, on the mesomorphic properties in their pure or mixed states. The mesophase behavior was investigated via differential scanning calorimetry, DSC, and mesophases identified by polarized light microscopy, PLM.

1. Introduction

It is already known that the mesomorphic properties of nematic mesogens are strongly influenced when a lateral group is appended to a nematic core. The extent of such effect is dependent on the size, position, and polarity of the lateral substituent. Sterically, a lateral substituent effectively widens the core and increases the intermolecular separation. This leads to a reduction in the lateral interactions [1–3] and, hence, the nematic stability is reduced. Gray [4] has explained that an increase in the breadth of the molecules reduces the stability of both the nematic and smectic mesophases. On the other hand, different positions of the lateral substituent result in the protrusion of the side group with different angles. For example, the mesomorphic properties of 2-(4-(4-n-alkyloxy benzoyloxy)-2- (or 3-) chloro phenylazo naphthalines were compared [5] to evaluate the effect of the position of lateral chlorine atom on mesomorphism. Finally, the polar lateral group affects each of the lateral polarizability and the lateral dipole moment of the molecule to an extent dependent on its position and polarity. This is definitely reflected on the mesomorphic characteristics of the resultant molecule.

The goal of the present investigation is to measure the dipole moments of the previously prepared [6] di-laterally substituted homologous series (**I***n*$_{a-d}$) aiming to deduce, firstly, the most probable conformation for each of the differently, laterally, substituted analogues. Secondly, it is to relate the mesophase behavior of the compounds, in pure and mixed states, with the observed dipole moment (μ_{obs}) and consequently, the deduced conformations, as well as with their calculated longitudinal (μ_Y) and lateral (μ_X) dipole moments, and finally with the dipolar anisotropy of the molecule ($\Delta\mu = \mu_Y - \mu_X$).

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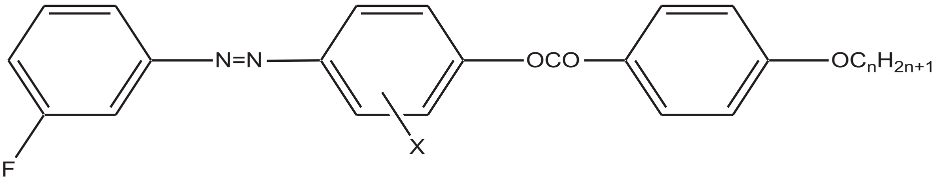


($\mathbf{I}n_{a\text{-}d}$)

$\mathbf{I}n_a$, X= 2-CH_3; $\mathbf{I}n_b$, X=3-CH_3; $\mathbf{I}n_c$, X=2-Cl, and $\mathbf{I}n_d$; X=3-CN

2. Experimental

2.1. Preparation of materials

2.1.1. 4-(3′-Fluoro phenylazo)-2-(or 3-) substituted phenyl-4′′-alkoxybenzoates, $\mathbf{I}n_{a-e}$

These derivatives were prepared as described previously. The transition temperatures of the compounds were in good agreement with those reported [6].

2.2. Physical characterization

Calorimetric measurements were carried out using a PL-DSC of Polymer Laboratories, England. The instrument was calibrated for temperature, heat and heat flow according to the method recommended by Cammenga et al. [7]. The measurements were carried out for small samples (2–3 mg) placed in sealed aluminum pans. All thermograms have been achieved at a heating rate of 10 °C/min in inert atmosphere of nitrogen gas (10 mL/min).

Transition temperatures were checked and types of mesophases identified for compounds prepared with a standard polarized-light microscope (Wild, Germany), attached to a home made hot-stage. The temperature is measured by thermocouple attached to a Brookfield temperature controller, England.

For dipole moment determination, static dielectric constants (ε) were measured with a WTW-Dipolemeter type DM 01, Germany. Refractive indices were measured by an Abbe Refractometer, Bellinghame and Stanley limited, England.

2.3. Measurement of dipole moments

Analytical grade benzene was purified according to recommended procedure [8]. Since the dipole moments of all members of a homologous series are the same, independent of the length of the terminal alkoxy-chain (n), the dipole moments of the analogues $\mathbf{I}12_{a-d}$, for the reason of solubility in benzene, were experimentally determined as examples.

Five dilute solutions of the compound in benzene were prepared having weight fractions ranging from 10^{-3} to 10^{-2}. The dielectric constants, density, and refractive indices were measured at 30 °C, and the dipole moments were calculated as described earlier [9]. On the basis of the precisions in the measurements of dielectric constants (±0.0005), densities (±0.0001), refractive indices (±0.001), and solution concentrations (±0.02%), the dipole moment values obtained are believed reliable to ±0.05 D.

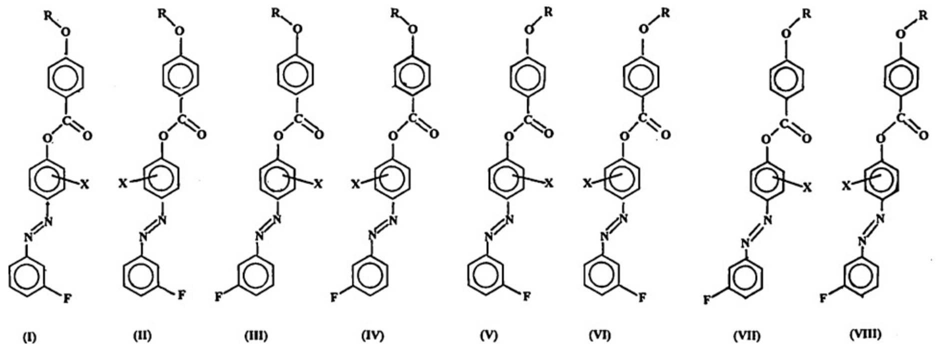
3. Results and discussion

3.1. Mesophase behavior and dipole moment

Since the mesophase stability of a liquid crystalline compound is mainly dependent upon the intermolecular attractions, in which molecular polarity plays a significant role, it has been shown [10] that in a series of compounds the dipole moment of any compound is dependent upon the nature of the substituent. It has also been shown [11,12] that the dipole moments of all members of a homol-

Table 1
Polarization data for compounds $\mathbf{I}12_{a-d}$.

Comp.	${}_DP_2$ (cm^3)	Graph.	Hedestrand				Palit–Ban		Guggenheim			μ_{obs} (D)
			$P_{2\infty}$	α	β	μ	γ	μ	Δ	α	μ	
$\mathbf{I}12_a$	206.0	1.72	254.0	2.54	0.76	1.68	1.94	1.71	0.59	0.76	1.65	1.69
$\mathbf{I}12_b$	174.0	4.42	672.6	5.05	0.02	4.70	0.72	4.30	4.33	5.05	4.58	4.50
$\mathbf{I}12_c$	243.1	2.45	313.4	1.89	0.01	2.40	0.47	2.22	4.58	1.89	2.53	2.40
$\mathbf{I}12_d$	221.0	5.60	1065	6.90	0.34	5.72	0.64	5.67	6.26	6.90	5.85	5.71



Scheme 1. Various possible planner conformations assigned for the homologous systems $\mathbf{I}n_{a-d}$.