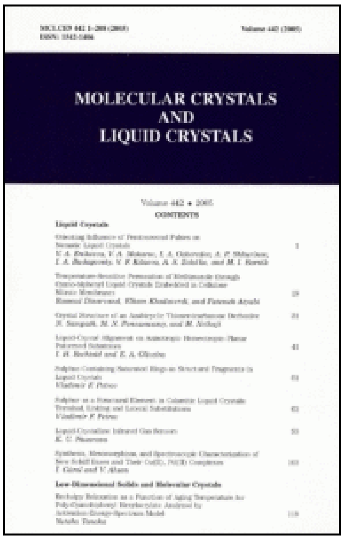

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

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To cite this Article Ajeetha, N. and Ojha, Durga P.(2010) 'The Influence of Oxygen on Mesomorphic Behavior of Benzylidene Anilines—The Effect of End Chain', Molecular Crystals and Liquid Crystals, 528: 1, 96 — 102

To link to this Article: DOI: 10.1080/15421406.2010.504619

URL: http://dx.doi.org/10.1080/15421406.2010.504619

Mol. Cryst. Liq. Cryst., Vol. 528: pp. 96–102, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.504619

The Influence of Oxygen on Mesomorphic Behavior of Benzylidene Anilines—The Effect of End Chain

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A variety of terminal chain modifications were made by placing/removing the electro-negative oxygen atom to either or both sides of the rigid core of the benzylidene aniline compounds, the chosen alkyl chain lengths were $n = 5$ *and* $m = 16$*. The mesomorphic properties were determined by polarizing thermal microscopy (TM) and differential scanning calorimetry (DSC). They exhibit two mono-variant and two di-variant phase sequences. The results are discussed in light of the depression in melting temperature, elevation of clearing temperature, and quenching of liquid-crystalline phases as a function of influence of oxygen with the end alkyl chain length.*

Keywords Benzylidene anilines; liquid-crystalline phase; terminal chain modification

Introduction

Liquid crystals (LCs) have become quintessential self-assembled materials of the modern era. The LC science and applications now permeate almost all segments of society from large industrial displays to individual homes and offices [1]. The scientific research devoted to liquid-crystalline materials has expanded greatly during the last several years. Of particular importance is the organic synthesis aspect to study the chemical, structural, and mesomorphic properties of compounds [2–4]. The mesomorphic behavior of liquid crystals is basically dependent on their molecular structures in which a slight change in their molecular geometry may bring about considerable change in their mesomorphic properties [5].

The liquid-crystal properties of the clearing temperature and enthalpy of transitions are influenced by the end chains. It is well known that physical and chemical properties of liquid-crystal molecules change with the length of end chains. In general, *trans* configurations have been used because they result in a more linear, rod-like molecular shape, a general requisite for the mesophase to occur. The Schiff's base compounds are *trans* and acoplanar. The existence of mesomorphic properties

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Address correspondence to Durga P. Ojha, Liquid Crystal Research Laboratory, Post-Graduate Department of Physics, Andhra Loyola College, Vijayawada-8, A.P., India. E-mail: durga_ojha@hotmail.com in these compounds is due to a twist in the aniline ring out of C–N=C–C plane and the calculations have indicated this twist to be as much as 55 degrees [6,7]. When two aromatic nuclei are not coplanar, it is possible for the terminal of one molecule to interact strongly with one of the rings of another molecule, causing additional attractions and a more thermally stable mesophase as the terminus grows in length [8].

The synthesis of liquid crystals containing terminal, linking, and lateral alkoxy groups plays an important role in display applications because of their promising physicochemical and electro-optical properties. The benzylidene aniline compounds are popularly known as *n*O.*m* compounds where *n* and *m* are flexible end chains. They constitute a series of compounds exhibiting rich polymesomorphism. In the present investigation, an attempt is made to address the influence of the position of oxygen on either side (*n*O.*m* or *n*.Om), on both sides (*n*O.O*m*), or in the absence of oxygen (*n*.*m*) to the essential rigid core where $n = 5$ and $m = 16$.

Experimental

The compounds were prepared by condensation of the corresponding benzaldehyde (0.1 mol) and aniline (0.1 mol) on refluxing with absolute ethanol in the presence of a few drops of glacial acetic acid [9]. After refluxing the reactants for 4 h, the solvent was removed by distillation under reduced pressure and the pure compound was recrystallized from absolute ethanol at low temperature. The schematic diagram explaining the synthesis of the respective compound is shown in Fig. 1.

The Textural Identification

The identification of polymesomorphic class is decided from evidence gleaned from several experimental sources, but microscopic textures of different smectic and nematic forms still remain and will remain a powerful and economically practical experimental means of classifying the smectic as well as nematic phase [10]. The changes in texture that occur at a phase transition are frequently important factor in phase identification. The optical textural observations [11] are made with an OLYMPUS DX 50 (USA) polarizing microscope equipped with a DP 10 CCD display, in conjunction with an INSTEC temperature controller (USA) of accuracy ±0.1°C.

Calorimetric Investigation

Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results; therefore, conclusions may be drawn concerning the nature of

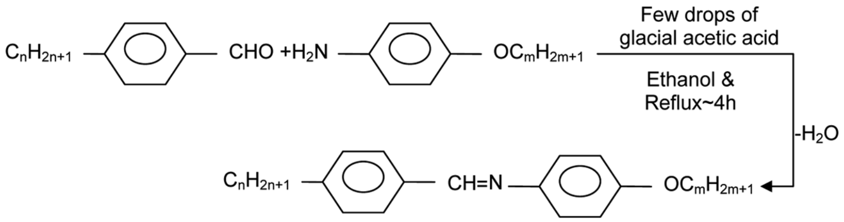

Figure 1. Schematic diagram explaining the synthesis of the *n*.O*m* compound where $n = 5$ and $m = 16$.

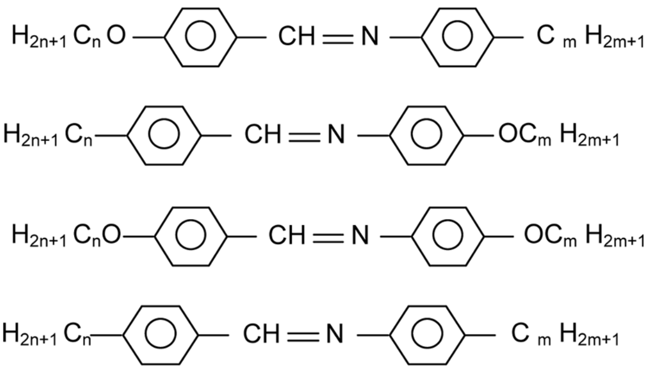

Figure 2. General molecular structure of benzylidene anilines with $n = 5$ and $m = 16$.

the phase that participates in the transition. The calorimetric investigations were carried out using a Perkin-Elmer DSC-7 instrument. The general molecular structure of benzylidene aniline compounds is shown in Fig. 2.

Results and Discussion

The phase characterization results of three compounds that differ in the presence (or absence) of an oxygen atom to the left and/or right of the rigid core of the benzylidene aniline are presented here. The phase variants exhibited by these compounds along with the phase transition temperatures and the heats of transition involved at the phase transformation are given in Table 1. The phase transition temperatures observed by thermal microscopy are found to be in agreement with those from the corresponding differential scanning calorimetry (DSC) thermograms shown in Fig. 3.

Although the optical textural observations reveal that these compounds exhibits traditional textures, they are found to exhibit two mono-variant and two di-variant sequenced systems. On cooling from the isotropic phase, the compound 5.O16 is found to grow a nematic phase exhibiting a threaded marble texture at 79.2°C, whereas in the case of 5.16 a smectic phase in the form of batonnets is seen at 52.9°C. This phase also exhibits a pseudo-isotropic texture in the homeotropic region, revealing it as an orthogonal phase (smectic-A). Further, with lowering of temperature, 5.O16 exhibits a smectic-G mosaic texture at 72.3°C (see Fig. 4).

This smectic-G phase is found to transform into a solid crystal phase on further cooling of the sample at 51.3°C. Similarly, the mono-variant 5.16 compound is found to transform the smectic-A phase to the solid crystal at 40.2°C on further cooling. The compound 5.16 exhibiting two peaks at 37.60°C and 34.02°C indicating the solid–solid transitions as evident from Fig. 3.

Role of Oxygen

Table 1 reveals that the position of oxygen plays a prominent role in determining the liquid crystallinity as well as the polymorphism of the compounds. The position of oxygen on either side of the rigid core favors the liquid-crystalline nature, and the absence causes a depression in melting temperature and a reduction of the liquid-crystal thermal range. But, an oxygen on both sides of the rigid core causes an

Table 1. Transition temperatures in °C along with the enthalpy values of N(4-*n*-pentyloxy benzylidene) 4′-*n*-hexa decyl aniline (5O.16), N(4-*n*-pentyl benzylidene) 4′-*n*-hexa decyloxy aniline (5.O16), N(4-*n*-pentyloxy benzylidene) 4′-*n*-hexa decycloxy aniline (5O.O16), and N(4-*n*-pentyl benzylidene) 4′-*n*-hexa decyl aniline (5.16) are shown

Compound name	Phase variant	Method		I-N/A	N-A	N/A-G	I/A/B-K		Ref.
5O.16	NA	TM	Cooling	68.8	67.4		55.1		[13]
5.O16	NG	DSC	Heating		78.25[a]		76.11[a]		
			ΔH.J/g			53.25			
			Cooling	74.49		69.98		60.33	
			ΔH.J/g	5.84		4.43		34.51	
		TM	Cooling	79.20		72.30		51.3	
5O.O16	N	DSC	Heating				97.66		
			ΔH.J/g				66.77		
			Cooling				85.63		
			ΔH.J/g				65.89		
		TM	Cooling	87.40			87.00		
5.16	A	DSC	Heating				50.80		
			ΔH.J/g				28.69		
			Cooling	48.27			37.60	34.02	
			ΔH.J/g	11.91			5.19	9.38	
		TM	Cooling	52.90			40.20		

[a] Peaks are not well resolved.

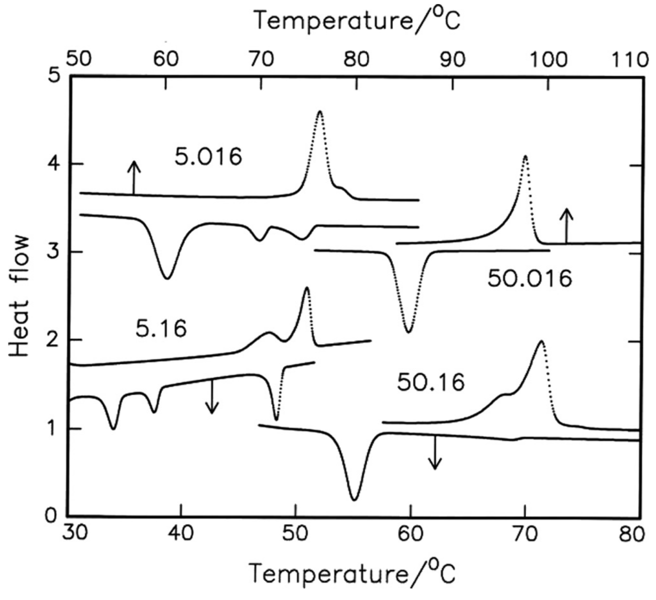

Figure 3. Comparative DSC heating and cooling thermograms of 5O.16, 5.O16, 5O.O16, and 5.16 compounds.

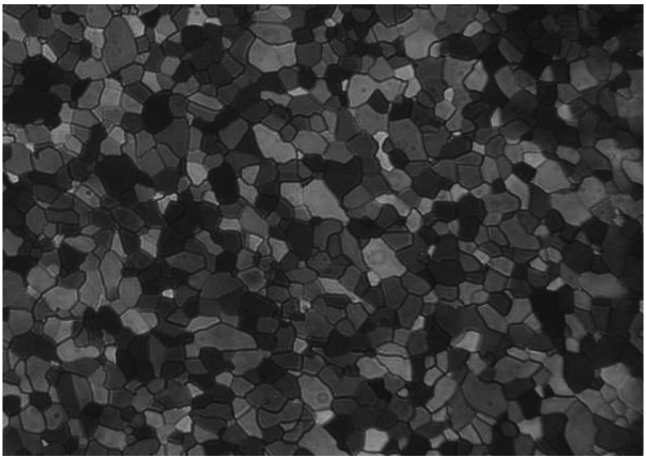

Figure 4. Smectic-G domain texture exhibited by 5.O16 compound on cooling at 72.3°C.

elevation in clearing temperature as well as the quenching of liquid-crystalline nature. A comparative picture of phase variants exhibited by the homologous series of N(4-*n*-alkoxy/alkyl benzylidene) 4′-*n*-hexa decyl/decyloxy anilines is presented in Table 2. Evidently, the fourth row (*n*O.O16) of the table infers that four compounds (except 5O.O16) exhibit no liquid-crystalline nature, accompanied by a direct transformation of isotropic liquid to solid crystal on cooling.

However, a narrow thermal range of about 0.4°C is observed in compound 5O.O16 that exhibits nematic phase through the exhibition of Schlieren texture on cooling (see Figure 5). In Figure 5, one may observe the simultaneous growth of solid and nematic Schlieren (four brushes) texture for which no traces are found even in the DSC thermograms at slow scan rates. It may be argued that the narrow range of the liquid-crystalline phase is dominated by the growth of the solid crystal phase from isotropic melt. Moreover, the oxygen on the aldehyde side is the most favorable condition for the mesophase.

The Effect of End Chain

Although oxygen plays a major role, the effect of the alkyl chain cannot be ruled out. Close observation of Table 2 reveals that even though the position of oxygen on

Table 2. Phase variants exhibited by *n*O.16, *n*.O16, *n*O.O16, and *n*.16 compounds with $n = 1$, 2, 4, 5, and 8

$n =$	1	2	4	5	8
*n*O.16	N	A	NA	NA	AB
n.O16	Non-LC	Non-LC		NG	Non-LC
*n*O.O16	Non-LC	Non-LC	Non-LC	N	Non-LC
n.16	Non-LC	Non-LC	A	A	Non-LC

The blank space indicates the compound yet to be reported.

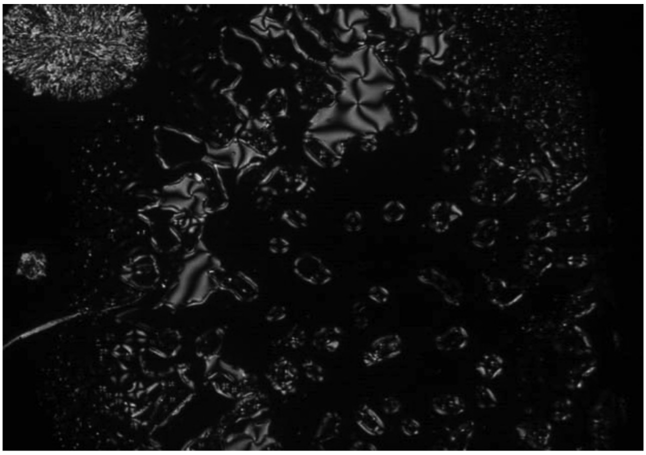

Figure 5. Simultaneous growth of nematic Schlieren texture and the solid crystalline phase exhibited by compound 5O.O16.

aldehyde is favorable, the lengths of the alkyl chain are also important in tuning the mesomorphism. In such a case, the middle homologous where $n = 4$ and 5, especially $n = 5$, is the most favorable series for the occurrence of the mesomorphism irrespective of oxygen.

Comparison with Other Homologous Series

The first row of Table 2 reveals that irrespective of chain length all the compounds exhibit mesomorphism because an alkoxy group is expected to pronounce the mesophase stability by its oxygen (with unshared-pair) overlap with the adjacent aromatic ring. While moving along each column, except the middle homologous ($n = 4$ and 5) members, all other lower and higher homologous series show a non-liquid-crystalline nature irrespective of the position of oxygen. It may be claimed that the repulsion between neighboring molecules with increasing intermolecular separation may responsible for these suppressed mesomorphic properties [12].

Conclusion

It may be concluded from the above discussion that the oxygen atom along with the longer alkyl chain length is less probable for the mesomorphism, whereas the oxygen atom in the aldehyde side is the most favorable condition for the occurrence of mesomorphism. However, the effect is prominently observed in the lower and the higher homologous series compared to the middle members.

Acknowledgment

The financial support rendered by the Council of Scientific & Industrial Research (CSIR), Department of Sciences & Technology (DST), University Grants Commission (UGC), New Delhi, and Department of Atomic Energy-Board of Research in Nuclear Sciences (DAE-BRNS), Mumbai, India, is gratefully acknowledged.

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