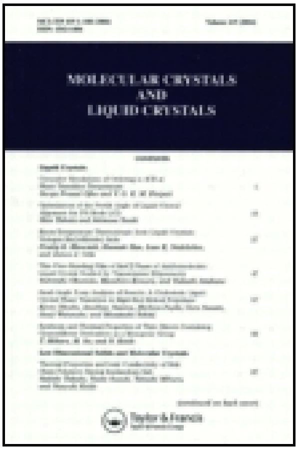

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Mesomorphic Properties of an Homologous Series of Alkoxy-Terminated Enamine-Ketone Containing Liquid Crystals

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An homologous series of enamine-ketone compounds has been synthesized and their thermal properties investigated. The bis [3-*p*-*n*-alkoxyanilino)-2-butenoyl] benzenes exhibited nematic mesophases when the terminal alkoxy substituents were short and both nematic and smectic mesophases when the terminal alkoxy substituents contained twelve or more carbons. The thermal data indicate that although crystalline order is largely determined by the packing of the hydrocarbon tails, there is a low degree of interaction by the tails in the nematic mesophase.

INTRODUCTION

In previous papers, it was reported that compounds containing hydrogen bonding enamine-ketone rings formed liquid crystalline phases.[1,2] Rigid rod model compounds comprised of enamine-ketone and phenyl rings displayed lower melting points and increased solubilities than the analogous all phenyl ring oligomeric polyphenyls. An homologous series with flexible aliphatic chains extending from a rigid core composed of phenyl and enamine-ketone rings also displayed nematic phases. The thermal data indicated that there is a low degree of interaction of

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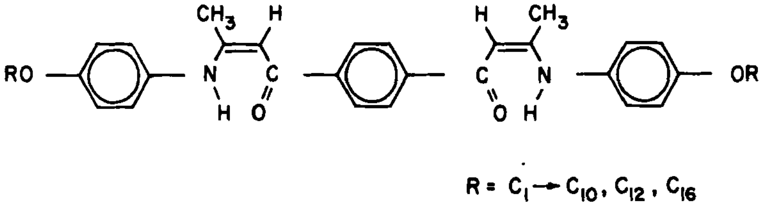
the alkyl chains in the nematic mesophase and the alkyl chains contribute little to the nematic mesophase order.

In order to learn more about this new class of liquid crystalline materials, the bis [3-(*p*-*n*-alkoxyanilino)-2-butenoyl] benzenes, of the following general structure, were synthesized and their thermal properties investigated.



EXPERIMENTAL

All compounds were synthesized and purified as detailed in an earlier publication.[2] The thermal properties were investigated using a Du Pont 990 Thermal Analyzer equipped with a DTA/DSC cell by a procedure, the details of which were also given earlier. Mesophase textures were observed via thermal optical analysis which aided in identification of mesophase type and provided a check on the transition temperatures.

RESULTS AND DISCUSSION

Crystalline Phases

In this series the methoxy through decyloxy, dodecyloxy and hexadecyloxy homologues were synthesized. The notation OC_n will be used to refer to the individual homologues, where *n* is the number of carbon atoms in the flexible chain. All of the compounds exhibited a nematic mesophase with the OC_{12} and OC_{16} homologues additionally exhibiting a smectic phase. Solid polymorphism was also present in several members of the series. There was a larger than normal exothermal shift in the baseline at the nematic → isotropic transition (256°C) of the OC_4 homologue which indicates that there may be a large difference in heat capacity between the nematic liquid and the isotropic liquid. The reason that this would be true for this compound and not other members in the series is not apparent.

Two solid phases were detected in the OC_5 homologue. The low temperature solid → solid endothermal transition at 129°C was followed by a slight exotherm and then melting into the nematic phase at 144°C. When the sample was cooled and reheated, the first endothermal peak was found at slightly lower temperatures and was larger in area. The second endotherm was found at the same temperature but was not as large as compared to the first scan.

Two crystal forms were also detected in the OC_7 compound which appeared at lower temperatures on the cooling scan due to supercooling effects. Reheating the sample resulted in lowering the first transition from 116°C to 85°C and lowering the second transition (solid → nematic) from 139°C to 132°C while their areas remained approximately the same for the two runs. As only 24 hours was allowed between runs, the lowering of the temperatures may be due to non-equilibrium states. Alternatively, these results may reflect the differences between a solvent recrystallized (first run) and melt crystallized (second run) samples.

The compounds OC_8 and OC_9 showed two crystal forms. The solid → solid transitions in these compounds were characterized by very small heats of transition and thus appeared almost as baseline shifts resulting from differences in heat capacities of the two solids. They occurred over a wide temperature range on heating but were much sharper on the cooling scans. These transitions were also detected by the thermal optical analyzer.

The OC_{10} compound produced three crystal forms. All of the transitions that were found during heating also appeared on cooling with supercooling effects noticed for the nematic → solid and solid → solid transitions. A smectic phase may have appeared on cooling from the nematic phase, as evidenced by microscopic observations, but crystallization followed so rapidly that it was difficult to confirm this.

The compounds OC_{12} and OC_{16} exhibited multiple solid → solid transitions and a smectic mesophase in addition to a nematic mesophase. The solid → smectic transition for OC_{12} was fairly broad and was resolved into two peaks during cooling of the sample. The phase transitions of OC_{16} are much more compact than OC_{12} and, as a result, individual peak measurement was difficult. Since it is instructive to look at the summed enthalpy and entropy changes of all crystal forms from 0°K to the melting of the compound, the area of this multiple peak was measured as a whole and an average temperature of 125.5°C was used as the transition temperature in the calculation of the entropy change. The smectic → nematic and nematic → isotropic transitions were also more compact in OC_{16}, occurring only 2°C apart. These were measured individually by constructing a vertical line from the minimum between the two transition endotherms to the baseline. This may result in a slight positive error in evaluating the heat of the smectic → nematic transition. Despite this extrapolation error, it is quite clear that the smectic → nematic peak area is larger than the nematic → isotropic peak area in OC_{16} in contrast to OC_{12} where the peak areas of these transitions are approximately equal. The smectic phase in both compounds has been identified as a smectic C by isomorphism with known liquid crystalline compounds.

Solid → solid polymorphism is common to mesogenic compounds and can be of two different types. In one type, there is no conversion between solid phases without first passing through the mesophase. In the second type, there is a solid → solid phase transition with equilibrium between solid phases. The solid phase behavior of the compounds in this series indicates that they belong to the second category and there is equilibrium between the solid phases.

Thermal Relations within the Series

A plot of the transition temperatures versus the number of carbon atoms in the alkoxy chains is shown in Figure 1. The thermal data for this series is given in Table I. Similar to the series in which the alkyl chains are bonded directly to the rigid core,[2] an odd/even alternation is present in the solid → nematic transition and apparently absent from

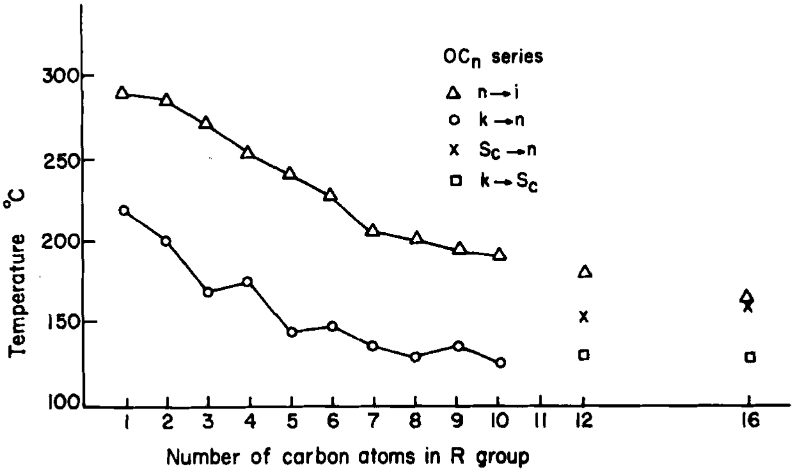


FIGURE 1 Transition temperatures versus the number of carbon atoms in the flexible chains in the OC_n series.

TABLE I

Thermodynamic Data for the bis [3-(*p*-*n*-alkoxyanilino)-2-butenoyl] benzenes

Compound	Transition	T, °C	ΔH x 10^4, cal/mole	ΔS, cal/mole/°K
OC$_1$	$K \rightarrow n$	218	1.21	24.6
	$n \rightarrow i$	288	.068	1.21
OC$_2$	$K \rightarrow n$	201	1.37	29.0
	$n \rightarrow i$	284	.084	1.51
OC$_3$	$K \rightarrow n$	168	.984	22.3
	$n \rightarrow i$	271	.053	.974
OC$_4$	$K \rightarrow n$	177	1.20	26.6
	$n \rightarrow i$	256	.074	1.40
OC$_5$	$K_I \rightarrow K_{II}$	129	.111	2.75
	$K_{II} \rightarrow n$	144	1.25	29.9
	$n \rightarrow i$	237	.053	1.04
OC$_6$	$K \rightarrow n$	147	1.05	25.0
	$n \rightarrow i$	227	.066	1.32
OC$_7$	$K_I \rightarrow K_{II}$	116	.194	4.98
	$K_{II} \rightarrow n$	139	1.15	27.9
	$n \rightarrow i$	209	.048	.996
OC$_8$	$K_I \rightarrow K_{II}$	84	.072	2.02
	$K_{II} \rightarrow n$	130	1.18	29.3
	$n \rightarrow i$	206	.052	1.09
OC$_9$	$K_I \rightarrow K_{II}$	92	—	—
	$K_{II} \rightarrow n$	139	1.16	28.1
	$n \rightarrow i$	195	.048	1.02
OC$_{10}$	$K_I \rightarrow K_{II}$	94	.050	1.38
	$K_{II} \rightarrow K_{III}$	121	.236	5.99
	$K_{III} \rightarrow n$	125	.908	22.8
	$n \rightarrow i$	189	.043	.931
OC$_{12}$	$K_I \rightarrow K_{II}$	84	—	—
	$K_{II} \rightarrow K_{III}$	110	.412	10.8
	$K_{III} \rightarrow K_{IV}$	118	.098	2.50
	$K_{IV} \rightarrow s$	127	1.06	26.5
	$s \rightarrow n$	151	.042	.99
	$n \rightarrow i$	180	.048	1.06
OC$_{16}$	$K_I \rightarrow K_{II}$	118	1.76	59.0
	$K_{II} \rightarrow K_{III}$	124		
	$K_{III} \rightarrow s$	127		
	$s \rightarrow n$	160	.134	3.09
	$n \rightarrow i$	162	.076	1.75

the nematic → isotropic transition. At longer alkoxy chain lengths, the nematic phase stability range decreases concurrently with an increase in the smectic phase stability range. This behavior is common to liquid crystal homologous series and often the nematic phase disappears completely with the smectic phase melting directly into the isotropic liquid.[3-5] It would seem from Figure 1 that the OC_{16} homologue is almost at this point. Comparison of the transition temperatures for this series with the series previously reported in which the alkyl chains are bonded directly to the rigid core[2] shows that the alkoxy series tends to exhibit higher melting points and polymorphic behavior. The oxygen linkage enhances the stability of the alkoxy series by increasing the polarizability of the molecule which accounts for the higher melting temperatures. This is a well documented phenomenon and occurs in many homologous series.[3,4,6,7]

The enthalpy (ΔH) and entropy (ΔS) changes for the transitions in the alkoxy series are plotted as a function of the carbon chain length in Figures 2 and 3, respectively. When plotting the solid → mesophase transition enthalpy and entropy of these compounds, the value used is the summed enthalpy and entropy of transition for all crystal forms detected. Barrall and Johnson[7] have cited the importance in using the summed entropy of transition for all crystal forms which are stable between 0°K and the transition temperature when considering the entropy of the solid → mesophase transitions. This point has been demonstrated for other transitions in organic compounds and is probably necessary in order to observe regular trends.[8]

Figures 2 and 3 show that there is an odd/even alternation in the solid → mesophase transition enthalpies and entropies when plotted as a function of the alkoxy chain length. Dewar and Griffin[9] have shown that transition temperatures and, in some cases, heats of transition may lack correlation and demonstrate the importance in considering the change in entropy. However, both ΔH and ΔS follow quite similar patterns in this enamine-ketone series. Analysis of the data of the solid → mesophase transition results in finding two groups of data. The compounds in which only one crystal form was detected, $OC_1 \rightarrow OC_4$, OC_6 have entropy changes that are, on the average, 5 cal/mole/°K lower than the compounds in which two or more crystal forms were detected, OC_5, $OC_7 \rightarrow OC_{10}$. From the previous discussion, it seems probable that not all crystal forms have been detected.

For the homologous series in which the hydrocarbon chains were linked directly to the core,[2] it was shown that the mesophase order was most dependent on the rigid core while the aliphatic chains played a

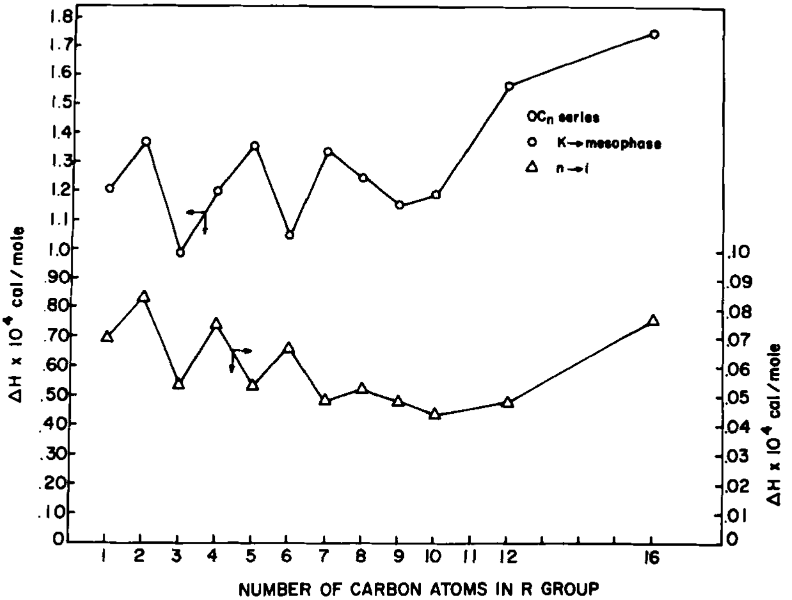


FIGURE 2 Enthalpy change (Δ*H*) for the phase transitions versus number of carbon atoms in the flexible chains in the OC_n series.

more important role in the crystalline packing of the solid phase. Similar conclusions are made about the importance of the aliphatic chains in the crystalline packing for the OC_n series. This is clearly evident at longer chain lengths when the entropy change increases dramatically. Figures 2 and 3 show that the solid → mesophase enthalpy and entropy changes increase as the hydrocarbon tail length increases. However, this is not true for the nematic → isotropic transition. The nematic → isotropic enthalpy and entropy change is essentially constant over the complete range of chain lengths. This suggests a low degree of interaction for the flexible chains in the nematic phase and indicates that the chains are free to rotate as in the isotropic liquid. Although the chains are not laterally associated, they may determine which of two possible arrangements neighboring enamine-ketone nuclei can adopt in order to account for the odd/even effect. The interchain order is still relatively low at OC_{16}. The low degree of alkyl chain interaction has been observed occasionally in other systems.[7]

It was previously pointed out that the usual odd/even effect is absent in the nematic → isotropic transition temperatures. Although the nematic → isotropic transition temperatures are traditionally used to an-

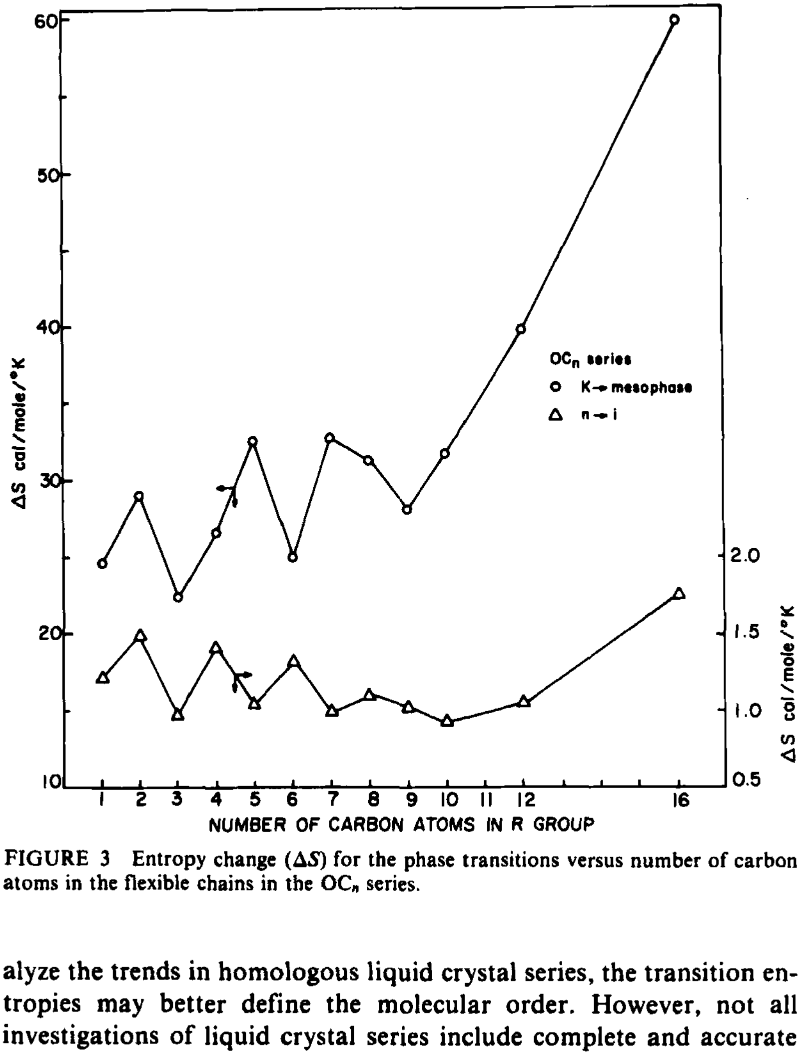


FIGURE 3 Entropy change (ΔS) for the phase transitions versus number of carbon atoms in the flexible chains in the OC_n series.

alyze the trends in homologous liquid crystal series, the transition entropies may better define the molecular order. However, not all investigations of liquid crystal series include complete and accurate data on enthalpy and entropy changes. The odd/even alternation in transition temperatures may be too small to detect in this homologous series. Certainly not all homologous series display the same degree of alternation in transition temperatures. Other series, such as the 4-ethoxy-4′-*n*-alkanoyloxyazobenzenes, display a much more marked alternation in the nematic → isotropic transition entropies with chain length than in the nematic → isotropic transition temperatures.[10] The use of transition enthalpies and entropies as additional tools to study the trends in homologous series should be encouraged.

Table II contains the thermodynamic data for three compounds which differ in the oxygen content of the flexible chain. The data for the first and second compounds has already been presented and is included in the table for comparison purposes. The last compound in the table has the same five ring core as C_8 and OC_7, but has *p*-2-(2-methoxyethoxy) ethoxy chains extending from the ends the core. Hence, it is possible to examine the effect of ether linkages in the flexible tails as these compounds differ only in this respect. The compound OC_7 has a much wider mesophase stability range (70°C) than compound C_8 (18°C). Also, the nematic → isotropic enthalpy and entropy changes for OC_7 are slightly larger than for C_8. These data suggest greater mesophase stability and order for OC_7. This is not surprising for the reasons discussed previously and can be seen in general comparisons between the C_n and OC_n homologous series. On this basis, it might be assumed that increasing the oxygen linkages would further increase the stability and order in the nematic mesophase. The data for the compound with *p*-2-(2-methoxyethoxy) ethoxy chains shows this is not true. The nematic → isotropic entropy change for this compound is substantially less than for C_8 or OC_7 and the temperature range over which the nematic mesophase is stable decreases from 70°C for OC_7 to 51°C for the compound with two additional oxygen linkages. When an ether linkage is substituted for a methylene next to an aromatic ring, the resonance of the ether linkage with the ring produces a dipole in the direction of the long axis of the molecule. The conjugative interactions would result in a more stable mesophase. However, when the ether linkage is not conjugated with an aromatic ring, the dipole produced is at

TABLE II

Thermodynamic Data for Enamine-ketone Compounds with Differing Oxygen Content in the Flexible Chains

Cmpd	Transition	T,°C	ΔH x 10^4,cal/mole	ΔS, cal/mole/°K
C_8	K → n	157	1.38	32.1
	n → i	175	.042	.937
OC_7	$K_{I} \rightarrow K_{II}$	116	.194	4.98
	$K_{II} \rightarrow n$	139	1.15	27.9
	n → i,	209	.048	.996
$OC_2OC_2OC_1$	K → n	129	1.40	34.8
	n → i	180	.034	.75

some angle to the long axis of the molecule and will generally destabilize the mesophase.[11] The data in Table II supports this interpretation.

CONCLUSIONS

Hydrogen-bonding rings containing heteroatoms have been used in the synthesis of new liquid crystalline materials. These compounds exhibit both smectic and nematic mesophases which are stable over wide temperature ranges. The thermal data indicate that the flexible chains extending from the end of the core do not contribute to the order of the nematic mesophase and are essentially free to rotate as in the isotropic liquid. The crystalline order in the solid phase seems to be more dependent on the packing of the flexible tails. It was also shown that ether linkages tend to stabilize the nematic mesophase when conjugated with an aromatic ring but unconjugated ether linkages exhibit the opposite effect, probably due to the transverse dipole which is created.

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