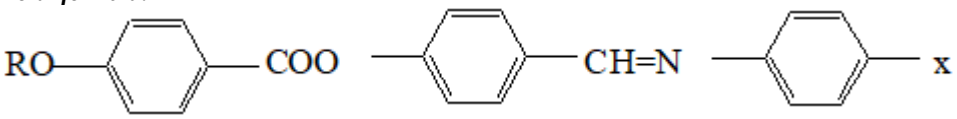
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The Syntheses of Compound Derived (4-butyloxy benzoyloxy) benzaldehyd and Study of these Liquid Crystalline Behavior

Suad Abdul Muttalib Mohammed

Department of Techniques Chemical Industries-Institute of Technology / Baghdad, Middle Technical University

Abstract: ***Preparation series of liquid crystalline Schiff base Butyloxybenzoyloxy) benzaldehyde and -derived from 4–(4 various substituted anilines, having the general formula:***



R1 X=I,F R=C_1-C_4
R2 X=CH_3 R=C1-C_4

The characterization of the compounds was achieved by different spectroscopic methods, e.g., UV, IR, 1H-NMR and Mass spectroscopy. The reflects the result of the mesomorphic study (by differential scanning calorimetry and polarized optical microscopy) carried out on the prepared compounds .It has been found that the compounds (R1$_5$, R2) are enanotiotropicnematogens The nematic range exhibited by these compounds follows the order (R1>R2)The enthalpy and entropy changes for the various transitions are calculated and reported Miscibility experiments were carried out on three (two - component) systems and their liquid crystalline behaviour was studied by polarized optical microscopy . the phase diagrams of the binary systems are reported which reveal that Thebinary systems (R1+R2) formed simpleneutectic mixtures and remained enantiotropicnematogens .

1. Introduction

Liquid crystal (LC) phases represent a unique state of matter characterized by both mobility and order on a molecular and at the supramolecular levels. This behaviour appears under given conditions, when phases with a characteristic order intermediate to that of a three dimensionally ordered solid and a completely disordered liquid are formed. Molecules in the crystalline state possess orientational and three dimensional positional orders. That is the constituent molecules of highly structured solids occupy specific sites in a three dimensional lattice and points their axes in fixed directions as illustrated in Fig.1.1a. Liquid crystal phases possess orientational order (tendency of the molecules to point along a common direction called the director **n**) and in some cases positional order in one or two dimensions as shown in Fig I.1b and I.1c. On the other hand, in the isotropic liquid state, the molecules move randomly and rotate freely about all possible directions (see Fig. I.1d). Thus, liquid crystals (LCs) have been defined as "orientationally ordered liquids" or "positionally disordered crystals" that combine the properties of both the crystalline (optical and electrical anisotropy) and the liquid (molecular mobility and fluidity) states [1]

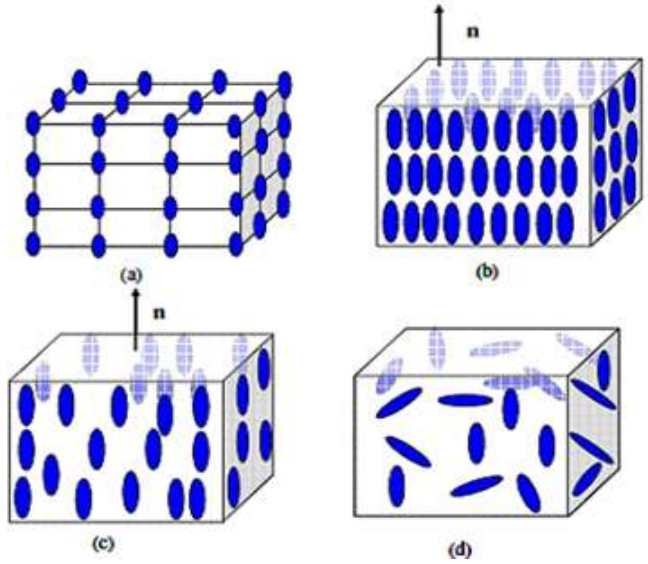


Figure 1.1: Schematic representation of molecular packing in the a) crystals b & c) liquid crystals and d) liquid state

2. Experimental

2.1. *Synthesis* of *materiats*

Alkyloxybenzaldehydes, were synthesizedby adding a solution of 0.2mol of 4-hydroxybenzaldehyde in 100ml of methanol containing 0.1mol of KOH to 024mol of the appropriate alkyl bromide, in 40 ml ofmethanol and the mixture was heated under reflux with stirring for 30

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h. The mixture was cooled, the organic layer was separated and washed successively with 10ml of saturated NaHCO, and 10ml of H,O. The organic layer was dried over anhydrous Na,SO, and the solvent was removed on a rotary evaporator. The concentrate was applied to a silica gel column and the pure 4-alkyloxybenzaldehwas eluted with diethyl ether and recovered as an oily liquid on removal of the solvent **(4-alkyloxyphenyl)** thiazolodithiazoles, (in which the alkyl group is to(10, 12) were synthesized by adding 5mmol of the appropriate 4-alkyloxybenzaldehyde to 10mmol of dithio-oxamide in 10ml of ***N*** **,** ***N*** dimethylformamide and the reaction mixture was heated under reflux with stirring for 3h. The reaction mixture was cooled and the yellow crystalline product was collectedby filtration. The crude product was washed with ethanol and recrystallized from chloroform. All the prepared dithiazoles had satisfactory elemental analyses.

2.2. Spectral, optical and thermal characterization

IR spectra (KBr) were recorded on spectrometer. UVspectra were recorded on SP8-100 UV spectrophotometer. 'H NMRspectra were recorded on a Bruker WH-90 spectrometer. The phase transitions wereobserved with a LeitzLaborlux 12 Pol in conjuction with a Leitz 350 hot stage and equipped with a Vario-Orthomat camera. Differential scanning calorimetry resultswere recorded at a scan rate of 10"Cmin-' with a Stanton Redcroft**DSC** 700instrument.

3. Results and Discussion

All compounds exhibited intense IR absorptions at c. 1603 cm-' (C=C stretch) [9], 1500cm-' (C=N cyclic, stretch) [lo], and 1250cm-' (C-0-C, stretch). A medium absorption was also recorded at 3050cm (C=C-H unsaturated, stretch), 2930cm-(C-C--H saturated, stretch), 812-853 cm-' (p-substituted aromatic ring) and 685cm-' (C--S, stretch). The UV absorption spectra in chloroform of the compounds were identical and contained two bands with *A*,,, at 370 nm (log ***E*** =3.90) and 240nm (log~=4.45)(here ***E*** is the molar extinction coefficient). The **'H** NMR spectral data for the ATT, series of compounds show broadly similar spectral characteristics and the data for ATT, compound is representative of the series; 6 (CDCI,) 0.95(t, ***J*** =6.0 Hz, **6H, CH,),** 1.36*(rn*,16H), 1.84(m, 4 H), 4.05 (t, ***J*** =6.0 Hz, 4 **H,** 0-CH,), 7.0 (d, ***J***=**8.8** Hz, 4 H) and **7.97**ppm (d, ***J***=8.8 Hz, 4 H). The DSC scans carried out on these compounds show transitions at temperatures which are in agreement with those obtained with optical microscopy. These transition temperatures are given in table **1.** Among these compounds thermal reversibility was poor for the first two members of the series as they tend to decompose on heating close to the isotropic liquid. The DSC traces for the remaining compounds revealed well behaved phase transitions (see figure 1) which were reproducible on subsequent heatings (see figure 2).

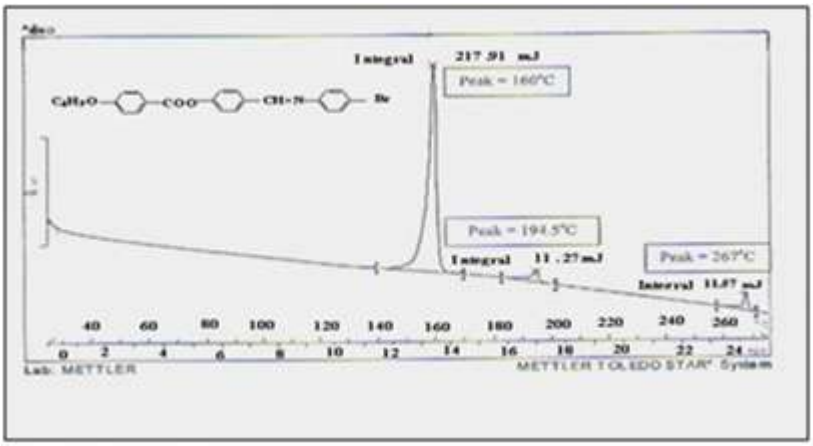


Figure 1: DSC trace for compound

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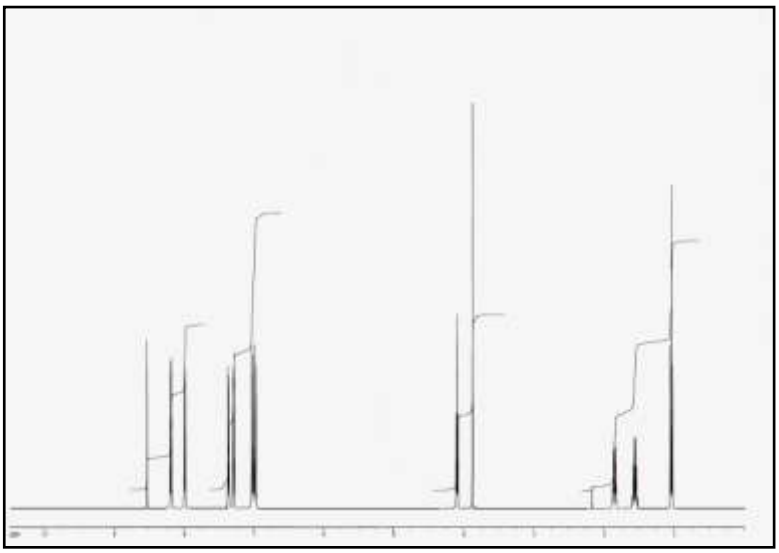


Figure 2: HNMR trace for the**,** compound

Table 1: Transition temperatures ("C)for the, series

Co.	*S_C – Total C C - N*			**Total S_C -- N**			**Total N - I**		
	T_{C-N} T_{C-SC}	HΔ J.Mol^{-1}.	S Δ *J.Mol^{-1}.k^{-1}*	T_{SC-N}	HΔ J.Mol^{-1}.	S Δ *J.Mol^{-1}.k^{-1}*	HΔ J.Mol^{-1}.	T_{N-I}	S Δ *J.Mol^{-1}.k^{-1}*
R1	158.1	36802	84.781				1648.0	280	3.1
R2	122	32638.4	78.9130				1836.30	301	3.1989
R_3	146	24521	56.609	194.	1273.1	2.7235	1307.2	267	2.4208
R_4	142.1	23789.	56.959	183.	867.61	1.8999	1305.0	269	2.409
R5	114.5	21898.	55.768					277	
R6	131	2786	69.21				1747.	255	3.3317

Several crystal-crystal transformations appear on **DSC** traces but they were not observed by optical microscopy. Each of the compounds **(n=3-10, 13)** exhibited one crystalxrystal transition with the exception **of** one homologue, ***n***=5, which displayed two crystal-crystal transformations. No such transformations were observed for the first three members, ***n***= 1 to **3, of** the series. Subsequent cooling and reheating cycles carried out **on** the same sample revealed slightly lower temperatures for these transitions (see figure 2). These transitions were not investigated further since we were primarily interested in mesomorphic transitions. The enthalpy and entropy values associated with these crystal-crystal transitions are presented in table 2. The enthalpy and entropy changes for the transitions in serieS are plotted as a function of the carbon chain length in figures 6 and 7, respectively. When plotting the crystal-mesophase transition enthalpy and entropy of these compounds, the value used **is** the summed enthalpy and entropy of transition for all crystal forms detected. Previous workers have cited the importance in using the summed entropy of transition for all the crystal forms which are stable between OK and the transition temperature when considering the entropy of the solid-mesophasetransitionS.

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