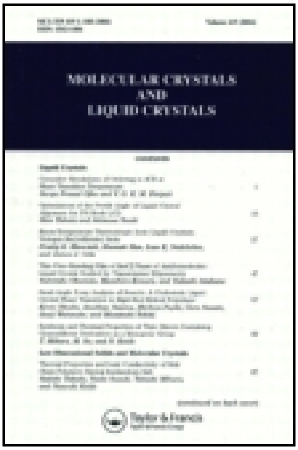

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Synthesis and Characterization of Mesogenic 1,3,4-Oxadiazole Derivatives

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A synthesis of homologous series of mesogenic 2-amino-5-alkkloxyphenyl-1,3,4-oxadiazoles were prepared by the oxidative cyclisation of alkyloxybenzaldehyde semicarbozones (4) using chloramines-T (CAT) as osidate via intramolecular cycloaddition reaction. The reaction proceeds in better yield (75–85%) giving the product as solid with low melting points. The optical texture studies have been carried out using Leitz polarizing microscope to identify the liquid crystalline phases at different temperatures and it is found that the synthesized compounds exhibit nematic (N), smectic C (Sm C), smectic I (Sm I) and smectic G (Sm G) phases, sequentially at different temperatures.

Keywords: homologous series; mesogenic; synthesis

INTRODUCTION

Girdziunaite *et al.* [1] synthesized 2-(4-alkylcyclohexyl) and 2-alkylthio-5-(4-hydroxyphenyl)-1,3,4-oxadiazoles with wide mesomorphic ranges. Recently Semmler and Co-workers [2] have reported non-linear mesomorphic liquid crystalline ester of 2,5-*bis* (4-hydroxyphenyl)-1,3,4-oxadiazoles. Hetzheim have investigated [3] the dielectric properties of three homologous series of 2-alkylthio-5-phenyl-1,3,4-oxadiazole derivatives and observed the nematic, smectic A and smectic C liquid crystalline phases depending on the chain

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length. During the last twenty years, a large number of mesomorphic compounds containing heterocyclic units have been synthesized [1,4,5]. Gallardo and Begnini [6] stated that the compounds having 1,3,4-thiadiazole rings show enantiotropic phases over intervals of about 100°C. However, the corresponding compounds with 1,3,4-oxadiazole rings are not mesomorphic and this behavior is related to the larger molecules curvature caused by the 1,3,4-oxadiazole rings. For the derivatives with 1,3,4-oxadiazole ring, where only the position of the oxygen heteroatom changes, mesomorphism returns although over smaller temperature intervals than with the derivatives of 1,3,4-thiadiazole. Again this behavior can be attributed to the molecular curvature produced by distribution of these heterocyclic rings.

Recently Xu *et al.* [7] synthesized some new liquid crystalline 2,5-disubstituted 1,3,4-thiadiazole derivatives as mesogenic unit. They observed that all 12 compounds are enantiotropic liquid crystals, and most of them exhibit nematic mesomorphism and broad smectic C mesomorphic ranges.

2-Amino and 2,5-diamino-1,3,4-oxadiazoles are formed by heating 1-acyl semicarbozones and substituted hydrazocarboxamides in excess of phosphorous oxychloride. Widely applied method for the synthesis of amino oxadiazoles involve the oxidative cyclisation of thiosemicarbozones or semicarbozones of aldehydes [8] in presence of an oxidizing agent such as lead oxide, bromine in acetic acid, bromine or iodine in aqueous sodium carbonate, hypohalites, Chloramine-T etc.

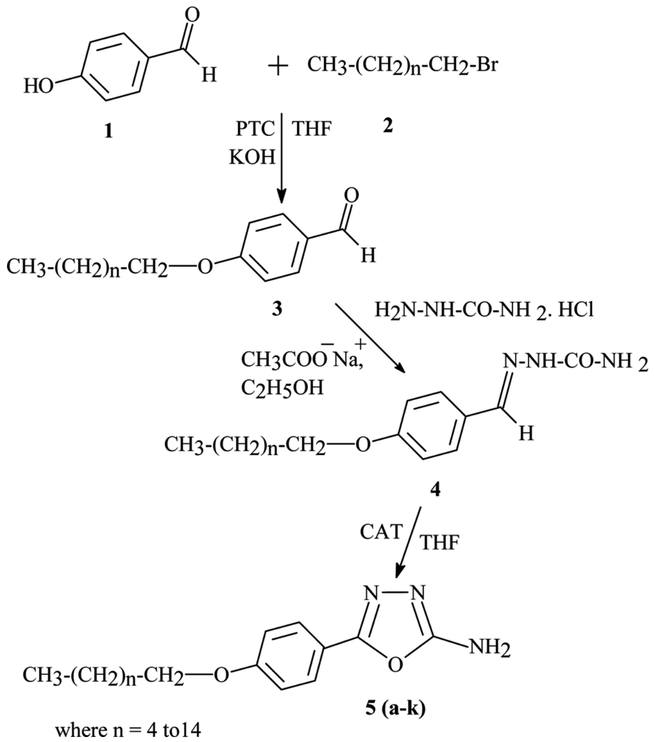
Karamyshava and Co-workers [9] showed that the substitution of polar groups like alkyloxy part in oxadiazole causes properties to the compounds. Recently Dingemans *et al.* [10] synthesized boomerang shaped liquid crystals based on 2,5-*bis* (*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) having a bond angle ~134° bend in the mesogenic cores. They found that substituting the nonlinear ODBP mesogenic core with P-dodecyloxyphenyl tails resulted in a non-linear mesogens, which exhibited five distinct mesophases and a clearing temperature of 204°C. The highest temperature phase appears to be nematic followed by a smectic C phase. The latter phase in freely suspended films does not appear to exhibit polar order. The highest temperature phase of 4,4′(1,3,4-oxadiazole-2,5-diaryl)-di-*p*-heptylbenzoate shows a schlieren texture with a 2-brush pattern exclusively. This and the above results prompted us to synthesize a new compound possessing 2-amino-1,3,4-oxadiazole ring containing alkyloxyphenyl group at position 5 (**5a–k**) and to study their mesogenic properties.

EXPERIMENTAL

General Synthetic Procedures

2-amino-5-alkyloxyphenyl-1,3,4-oxadiazoles (**5a–k**) was prepared by the oxidative cyclisation of alkyloxybenzaldehyde semicarbazones (**4**) using Chloramine-T as oxidant via intramolecular cycloaddition reaction. Smicarbazones were in turn prepared by the reaction of alkyloxybenzaldehydes (**3**) with smicarbazide hydrochloride. The starting material alkyloxybenzaldehydes were prepared from *p*-hydroxy benzaldehyde (**1**) with *n*-alkylbromide (**2**) in dry tetrahydrofuran (THF) in the presence of tetrabutylammoniumbromide as phase transfer catalyst (PTC) followed by treatment with powdered potassium hydroxide (Scheme 1).

1H NMR, 13C-NMR and mass spectral studies gave structure proof for the isolated products. In ^{1}H NMR spectra, the signal due to -CH_3 protons appears as broad singlet in the region δ 0.89–0.92 ppm., –$(CH_2)_n$-protons appear as multiplet in the region δ 1.30–1.49 ppm.,



SCHEME 1 2-amino-5-alkaloxyphenyl- 1,3,4,-oxadiazoles.

the $-NH_2$ peak appear as a singlet at δ 3.35–3.44 ppm., OCH_2 at δ 3.98–4.14 ppm. and aromatic protons at δ 7.04 and at 8.07 ppm. These observations support the formation of the cycloadducts. In ^{13}C NMR spectra, the $-C_2$ and C_5-carbon appear as singlet in the region δ 165.46–165.89 ppm and δ 162.39–162.59 ppm. respectively. The remaining ^{13}C carbon appeared in the expected region.

The mass spectrum of 1,3,4-oxadiazole **5e** did not show molecular ion peak, instead showed an ion corresponding to $M+1$, at m/e 318 as base peak. The $(M+1)$, ion at mass 318 should have formed by the abstraction of a hydrogen atom by the molecular ion from the neutral molecule. The radical ion at mass m/e 289 with relative abundance 75% could have formed from the base molecular ion m/e 318 by the loss of $-N_2$ molecule. The ion at m/e 275 was of 43% relative abundance formed by the loss of $-N{\equiv}C{-}NH_2$ (m/e 42) from the molecular ion. The molecular radical ion at m/e 259 with relative abundance 60% produced by the loss of molecular ion at m/e 58 with relative abundance 18%. The ion at m/e 233 with relative abundance 52% formed by the loss of ion at m/e 84 with relative abundance 24%. The base molecular ion m/e 318 could have yielded an ion at m/e 176 with relative abundance 80% by the loss of alkyl group $CH_3{-}(CH_2)_8{-}CH_2{-}$ m/e 141 have relative abundance 15%.

Typical procedure for the synthesis of 2-amino-5-(4-decyloxyphenyl)-1,3,4-oxadiazole (5e)

A mixture of 4-*n*-decyloxy benzaldehyde semicarbazone (**4e**, 1.2 g, 3.76 mmol) and CAT (1.08 g, 3.85 mmol) in THF (20 ml) was heated to reflux with stirring for 3 hours. Sodium chloride formed in the reaction was filtered off and washed with ethanol. The combined filtrate and washing were evaporated in vacuum. The residue was extracted into ether, washed with 10% sodium hydroxide (3 × 20 ml), brine solution and finally with water. The ethereal layer after drying over anhydrous sodium sulphate was evaporated in vacuum. The resultant residue was dissolved in chloroform (2 ml) and poured into a flask containing petroleum ether and the precipitate was collected and dried. Recrystallisation from ethanol gave oxadiazole as white crystalline solid in 83% (0.99 g) yield, m.p. 98–99°C.

Elemental analysis: $C_{18}H_{27}N_3O_2$ requires C 68.11, H 8.57, N 13.24; found C 68.01, H 8.47, N 13.20%.

Characterization of Materials

The purity of all the synthesized compounds was checked by thin layer chromatography using silica gel G. The final compounds were purified by column chromatography on silica gel (70–230 mesh, Merck) using chloroform-acetone (7:1) as the eluent. The yield of the compounds was in the range 75–85%.

The chemical structure of all the 2-amino-5-alkyloxyphenyl-1,3,4-oxadiazoles were confirmed by ^{1}H NMR spectra (Bruker 300 MHz spectrometer) as well as ^{13}C NMR spectra (Jeol GSX 400 spectrometer) with 1% tetramethylsilane in deuteriochloroform as an internal standard, Mass spectra were obtained on an electron impact Maspec MSW 9629 spectrometer and important fragments are given with the relative intensities in brackets.

In order to investigate the different properties of liquid crystals, the optical texture studies, DSC thermal analysis, X-ray and optical anisotropic studies have been carried out. The optical textures exhibited by the liquid crystalline compounds are studied using the polarizing microscope. The Leitz orthoplan-polarizing microscope is one of the important variants equipment for the observation of isotropic and anisotropic substances in polarized transmitted light.

The homogeneous specimen can be prepared by using a very clean glass slide and cover slip. Clean surfaces are obtained by soaking the glass in concentrated nitric acid for an hour, washing with distilled water, and finally rinsing with acetone which is then allowed to dry off and evaporate. For the optical texture studies, the liquid crystalline specimen has taken in the form of thin film in the order of 25 to 30 microns thickness between slide and cover glass. The textural changing with temperature is observed by using specially designed hot stage. The transition temperatures are measured by using platinum resistant thermometer or thermometer.

RESULTS AND DISCUSSION

Determination of Phase Transition Temperatures

The phase transition temperatures of the liquid crystalline compounds were determined using a polarizing microscope in conjunction with a conventional hot stage [11]. The transition temperatures of the specimen are varied across the transition points at the rate of 0.2°C per minute. Measurements were made using a calibrated thermometer graduated at the interval of 0.1°C or platinum resistance thermometer. The bulb of the thermometer was kept close to the specimen in order to ensure that there was no lag between the observed and actual temperatures. The phase transition temperatures of different compounds were shown in Table 1.

TABLE 1 The Phases Obtained at Different Temperature for the Series of Prepared Compounds

Compounds	Iso	N	Sm C	Sm I	Sm G
5a	136.0	59.6	56.2	—	—
5b	119.1	66.0	62.8	—	—
5c	104.5	73.2	70.1	—	—
5d	94.2	79.5	77.4	69.2	66.4
5e	86.2	85.8	84.5	75.7	73.1
5f	82.3	82.1	81.6	69.4	65.9
5g	79.8	79.5	77.3	63.2	—
5h	81.1	80.6	78.3	65.8	—
5i	83.0	81.7	79.1	—	—
5j	83.6	82.3	81.2	—	—
5k	84.9	83.5	83.0	—	—

Optical texture studies of 2-amino-5-alkyloxyphenyl-1,3,4-oxadiazoles

The homologous series of 2-amino-5-alkyloxyphenyl-1,3,4-oxadiazoles (**5a–k**) have been synthesized and these compounds exhibit nematic, smectic C, smectic I and smectic G phases sequentially shown below. The nematic mesophase for all compounds in this series, exhibit Schlieren texture and the typical nematic droplets on cooling the specimen from isotropic liquid.

$$\text{ISO} \xrightarrow{86.2^\circ\text{C}} \text{N} \xrightarrow{85.8^\circ\text{C}} \text{Sm C} \xrightarrow{84.5^\circ\text{C}} \text{Sm I} \xrightarrow{75.7^\circ\text{C}} \text{Sm G} \xrightarrow{73.1^\circ\text{C}} \text{Cry}$$

When the specimen is cooled from its isotropic melt at 86.2°C. It exhibits isogirs of nematic (N) drops with four brushes (Fig. 1). The

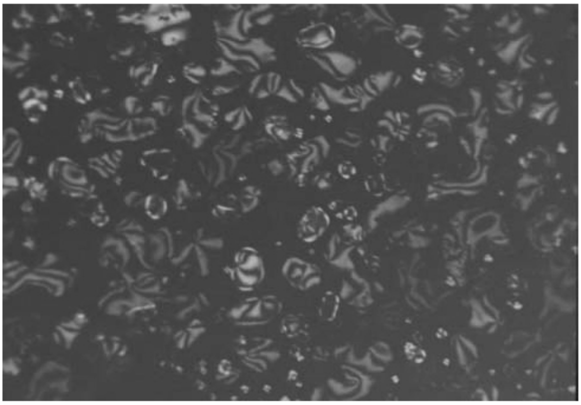


FIGURE 1 Isogirs of nematic (N) drops with four brushes (165×).

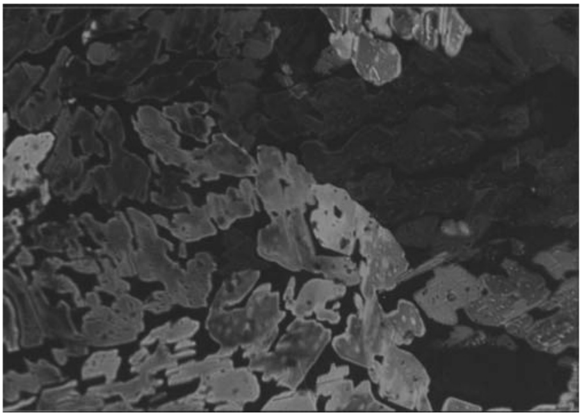


FIGURE 2 Mosaic texture of smectic I phase (135×).

brushes of the drops will rotate, when polarizer rotates along the same axis. These nematic drops collapse at temperature 85.8°C, then transformed into schlieren texture, which is characteristic of Sm C phase. On further cooling the specimen, nematic phase change over to Sm I phase at 84.5°C see Figure 2. This phase is a tilted biaxial phase, the pseudohexogonal molecular packing identifies the molecular structures in the smectic I phase and this phase is hexatic in nature. On further cooling smectic I phase transformed into striped pattern texture at 75.7°C which is characterized by Sm G phase see Figure 3. The molecules in this phase are packed in layers and with in the layers, molecules have their long axes tilted with respect to the normal

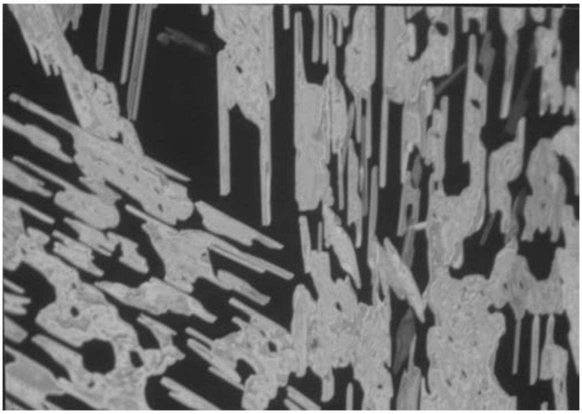


FIGURE 3 Striped pattern of G phase (135×).

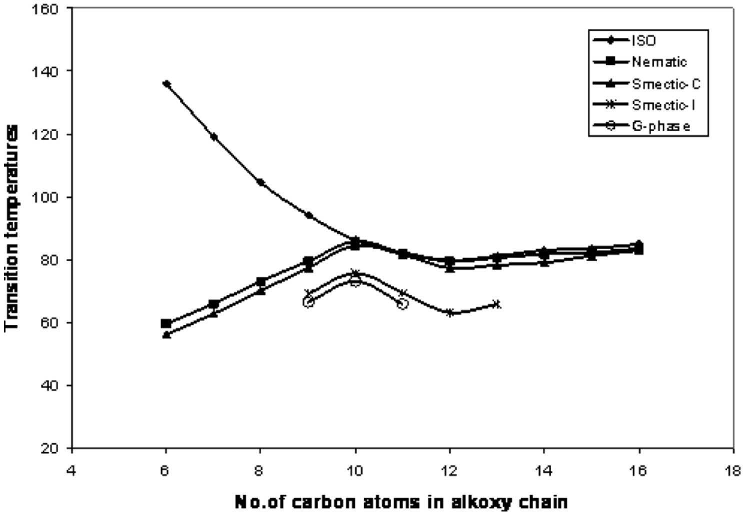


FIGURE 4 Plot of transition temperature versus the number of carbon atoms in the alkoxy chain..

to the molecular layer [12]. Finally, at 73.1°C the specimen changes over to crystalline phase. The transition temperatures recorded in DSC trace are in agreement with the transition temperature observed in optical texture studies and are given in Table 1.

A plot of transition temperature as a function of the number of carbon atoms (n) in the alkyloxy chain is shown in Figure 4. The first five members are monotropic nematic in nature and no odd-even effect has been observed. The nematic to isotropic curve shows the increasing tendency up to pentoxy derivative and then levels off. This behaviour has been discussed by Gray [13] for comparatively low melting series of liquid crystalline compounds.

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