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Synthesis and Characterization of a New Series of Liquid Crystal Compounds Derived from Isoxazoles

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Two homologous series of phenylisoxazoles derived from 3-[4-(4-trans-n-heptylcyclohexyl)phenyl]-5-(4-alkoxyphenyl)isoxazole and 3-[4-(4-trans-n-heptylcyclohexyl)phenyl]-5-(5-n-alkylthiophene)isoxazole have been synthesized. The liquid crystal compounds obtained were characterized by NMR, differential scanning calorimetry (DSC), and optical polarized microscopy (POM). The properties of the liquid crystalline phase were investigated as a function of terminal units and type of core aromatic rings. It was found that (1) the phase transition temperature decreased with the change of core aromatic rings from phenyl for thienyl, and (2) the types of mesophase formed by these compounds do not depend on the length of the terminal chain. Thermotropic nematic and smectic phases were observed.

Keywords Liquid crystals, isoxazole, mesophase

INTRODUCTION

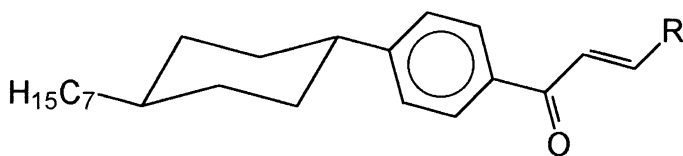
As a continuation of our study of the behavior of liquid crystal molecules containing five membered heterocyclic ring, we have now prepared and investigated the mesogenic properties of two homologous series of 3,5-disubstituted isoxazole. The synthetic intermediates were structurally characterized and the thermal behavior examined [1].

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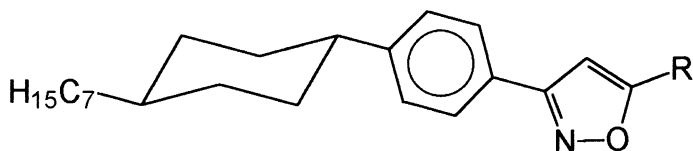
Address correspondence to Luciano da Silva, Engenharia de Computacao, Universidade do Vali do Itajaí, São José, SC, Brazil. E-mail:

In the course of our research program involving the synthesis of novel liquid crystals, we needed to use *trans*-1-(4-acetylphenyl)-4-*n*-heptylcyclohexane as a mesogenic subunit and β -diketones as a synthetic intermediate. The subunit phenylcyclohexane is present in large numbers of commercial liquid crystals, which generally leads to superior thermal, photo, and electrochemical stability and also to low melting points and viscosity [2, 3], β -Diketones are classic examples of precursors for the synthesis of mesogenic heterocycles or metallomesogenic derivatives [4]. Mesogenic isoxazoles and pyrazoles obtained via β -diketones have been described previously in the literature [5, 6]. In contrast, we describe the attainment of mesogenic isoxazoles through the use of α,β -unsaturated ketones. The isoxazole ring incorporates a strong dipole moment, and this effect could help increase the anisotropy of the polarizability and consequently favor mesogenic behavior [7]. In this work we have attempted to synthesize two families of α,β -unsaturated ketones (intermediates **1**, Series **I**) and their isoxazole derivatives (Series **II**). In order to study the influence of the molecular core on mesogenic properties, two differential rings have been introduced: 4-alkoxyphenyl and 5-alkythiophene. The mesogenic behavior of the compounds has been studied, and a comparative study of properties observed in the different derivatives has been included.

Série I



Série II



RESULTS AND DISCUSSION

Synthesis

Synthesis of α,β -unsaturated ketones

The most common procedure for the synthesis of α,β -unsaturated ketones is the classic Claisen-Schmidt reaction. The synthesis involves the condensation of the aromatic aldehydes with 4-[trans-4-n-heptylcyclohexyl] acetophenone in the presence of an aqueous alkali. There is a pronounced preference for the formation of *trans*-double bonds. This stereoselectivity is confirmed by ^1H NMR spectroscopy. The vinyl system AB shows two sets of doublets with $J_{\text{AB}} = 15\text{--}17$ Hz, which are typical values for the *trans*-vinyl system. In this reaction, all compounds formed under the conditions described are obtained in good yields. 4-[*Trans*-4-n-heptylcyclohexyl]acetophenone, 2-formyl-5-alkylthiophene and 4-alkoxybenzaldehyde were prepared according to the methods described in the literature [8–10]. The synthetic pathway to the target compounds **1** is depicted in Scheme 1.

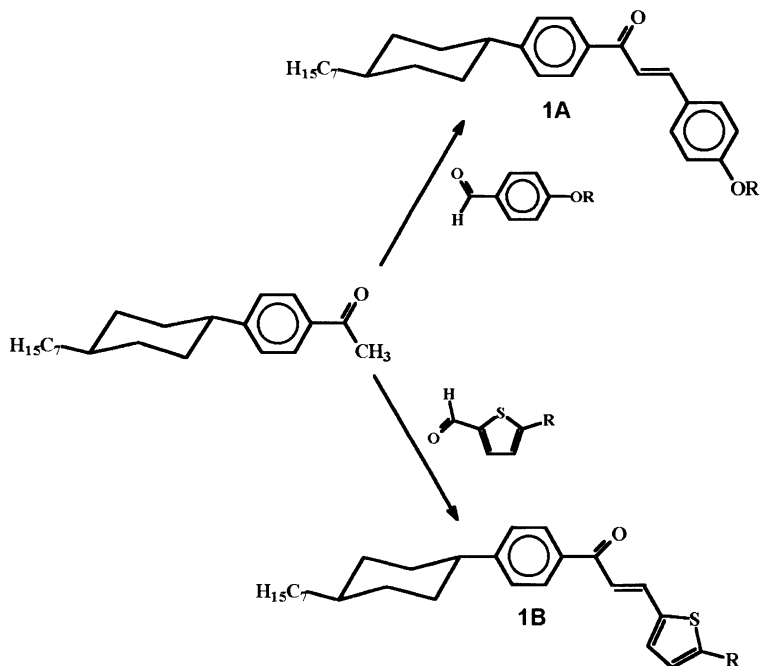
Synthesis of 3,5-diarylisoxazoles

This synthesis first involves the preparation of the α,β -unsaturated oximes from the reaction of α,β -unsaturated ketones with hydroxylamine hydrochloride [11]. In the subsequent reaction, the oxime is oxidized with tetrakis(pyridine)cobalt(II) dichromate (TPCD). This is a convenient procedure for the preparation of the 3,5-diarylisoxazoles in high yields. The synthetic pathway to the target compounds **2** is depicted in Scheme 2.

The structure of all target compounds and intermediates was confirmed by a combination of ^1H NMR, ^{13}C NMR (Bruker HX-200), and infrared spectroscopy (Perking-Elmer 783 IR spectrophotometer). The purity of the compound was evaluated by thin layer chromatography and elemental analysis. All of the data, summarized in the experimental section of this article, confirm the proposed structures.

Mesogenic Characterization

All of the compounds obtained were characterized after the synthetic and purification processes. All mesophases were identified according to their textures observed by optical microscopy, using the classification system reported by Sackmann and Demus, and Gray and Goodby [13, 14]. The optical and thermal data of α,β -unsaturated ketone intermediaries are given in Table 1. None of the α,β -unsaturated ketone intermediaries are



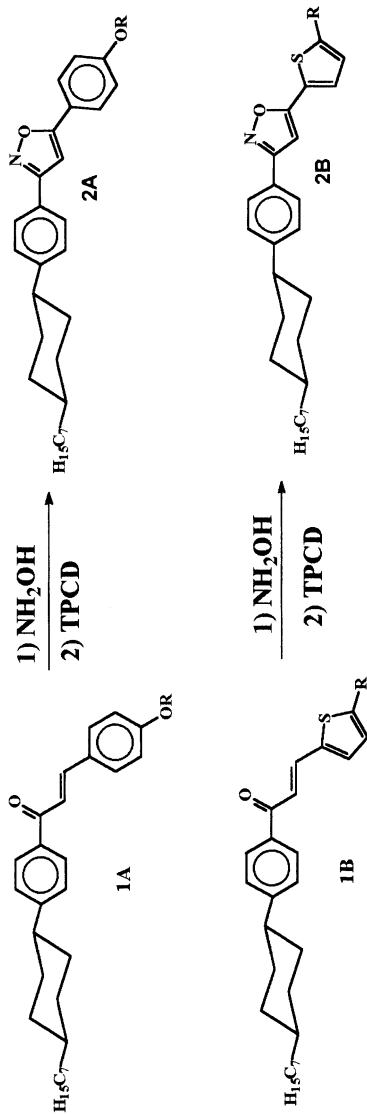
SCHEME 1 **1A1** R = CH₃; **1A2** R = C₇H₁₅; **1B1** R = H; **1B2** R = C₇H₁₅; **1A3** R = C₈H₁₇; **1A4** R = C₉H₁₈; **1B3** R = C₁₀H₂₁; **1B4** R = C₁₂H₂₅.

mesogenic. The replacement of alkoxyphenyl, thiophene, and alkylthiophene as linking groups with the intention of increasing the linearity of molecules did not result in the production of mesomorphism.

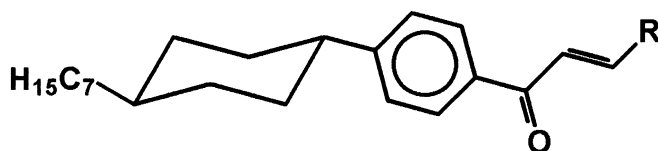
The behavior observed in these compounds can, in principle, be explained in terms of two effects:

1. The deviation from linearity of the linking group α,β -unsaturated ketone is in the order of 60 degrees, and the introduction of five membered heteroaromatic rings would only reduce the deviation to an angle in the order of 50 degrees.
2. Free rotation about the C-C single bond of the linking group α,β -unsaturated ketone, which can also permit the existence of conformational isomers that might destroy the anisotropy necessary for mesophase formation.

The separation of these two effects is necessary to better understand the relation between molecular structure and mesomorphic behavior. To study the



SCHEME 2 2A1 R = CH_3 ; 2A2 R = C_7H_{15} ; 2A3 R = C_8H_{17} ; 2A4 R = C_9H_{18} ; 2B1 R = H; 2B2 R = C_7H_{15} ; 2B3 R = $\text{C}_{10}\text{H}_{21}$; 2B4 R = $\text{C}_{12}\text{H}_{25}$.

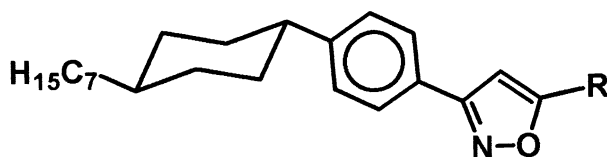
TABLE 1 Optical and thermal data α,β -unsaturated ketones 1-[4-(*trans*-4-n-heptylcyclohexyl)phenyl]-3-R-2-propen-1-one 1

Compound	Transition	Temperature ($^{\circ}\text{C}$)
1A1	C-I	95.0–97.0
1A2	C-I	110.0–112.0
1A3	C-I	109.0–111.0
1A4	C-I	98.0–100.0
1B1	C-I	92.0–94.0
1B2	C-I	85.0–87.0
1B3	C-I	84.0–86.0
1B4	C-I	83.0–85.0

interrelation between the two effects, compounds **2** were designed. These compounds minimize the effect of conformational isomerism but with linearity that in principle is equal to the α,β -unsaturated ketone intermediary. The optical, thermal, and corresponding enthalpy values of compounds **2** are given in Table 2. Transition enthalpies were determined by differential scanning calorimetry using a Perkin-Elmer DSC-2. The thermograms were recorded upon cooling at a rate of $5^{\circ}\text{C min}^{-1}$. All mesophases were identified according to their textures observed by optical microscopy. All compounds **2** are mesogenic. Nematic and smectic phases were observed. All compounds in this series exhibit enantiotropic phases. Once the isotropic liquid is cooled, a Schlieren texture allows us to identify a nematic phase. Once it is cooled further, a focal-conic texture appears in the S_A phase. This latter texture is easily transformed into a homeotropic texture by the application of mechanical stress. In compound **2A1** only a nematic phase was observed, and in compound **2B4** only a smectic A (S_A) phase was observed.

The principal characteristic observed in compounds **2** is the large thermal stability. This phenomenon is very common in mesogenic compounds that incorporate a strong transverse dipole moment. In this series, this behavior is attributed to the presence of isoxazole heterocyclic rings, which enhance the polarization of the molecules. These facts would explain the high clearing points observed.

In spite of the low melting point and molecular geometry of α,β -unsaturated ketones, none of the compounds of the intermediary series exhibit

TABLE 2 Optical, thermal, and thermodynamic data for 3-[4-(*trans*-4'-n-heptylcyclohexylphenyl)]-5-R-isoxazole 2

Compound	Transition	Temperature ($^{\circ}\text{C}$)	ΔH (KJ/mol)
2A1	C-N	135.0	25.04
	N-I	278.0	0.98
2A2	C-S _A	112.3	26.02
	S _A -N	225.3	1.20
2A3	N-I	234.0	1.12
	C-S _A	107.0	30.98
	S _A -N	221.9	1.58
2A4	N-I	229.1	1.00
	C-S _A	98.7	24.47
	S _A -N	223.0	1.87
	N-I	229.7	1.23
2B1	C-S _A	107.0	27.05
	S _A -N	130.0	1.32
	N-I	186.0	1.14
2B2	C-S _A	82.6	24.09
	S _A -N	165.2	1.81
	N-I	178.4	1.87
2B3	C-S _A	74.6	22.25
	S _A -N	168.0	1.74
	N-I	171.0	1.54
2B4	C-S _A	79.4	30.12
	S _A -I	166.8	4.95

mesogenic behavior. In these compounds, the length-to-breadth ratio is clearly low and doesn't favor the parallel molecular organization typical of the liquid crystal state. The deviation is from linearity to 27.4–25.7°. In contrast, the corresponding isoxazole derivatives have a more linear shape, with angle of only 10.7°.

The mesogenic behavior observed can be explained through the geometric and electronic factors associated with the molecular structure. The length-to-breadth ratio is greater in compounds of series **2** than those in series **1**, and consequently mesomorphism is favored. The enone linking groups disrupt the electronic conjugation between the aromatic group joined to the mesogenic core. In contrast, when the linking group is an isoxazole, the aromatic conjugation can be extended to the mesogenic core. This fact favors molecular planarity and also increases the anisotropy of electronic

polarizability, thus increasing molecular interaction (van der Waals forces) and consequently promoting liquid crystal behavior.

CONCLUSION

Two new series of the compounds were synthesized. The liquid crystal properties of these compounds were investigated. In general, the α,β -unsaturated ketones groups significantly increase the molecular width, making the parallel alignment of the molecules necessary for the achievement of mesomorphism difficult. Consequently, mesogenic behavior is only observed in the isoxazoles. This group allows for extended conjugation through the molecule and emphasizes the importance of electronic factors in mesophase formation.

EXPERIMENTAL SECTION

The transition temperatures for all compounds were determined by optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP 52 heating stage. The transition temperatures and enthalpies were determined using a Perkin-Elmer DSC-2 differential scanning calorimeter, which was calibrated by measuring the known melting point (429.6 K) and heat of fusion (28.46 KJ mol⁻¹) of indium. The heating and cooling rate was 10°C min⁻¹. The purity of the compounds was evaluated by thin layer chromatography and elemental analysis (Perkin-Elmer 2400). The IR spectra were recorded using KBr discs with a Perkin-Elmer 283 spectrometer, and the ¹H NMR and ¹³C-NMR spectra were recorded at 200 MHz (Bruker HX-200).

General Procedure for Preparation of the α,β -Unsaturated Ketones

Sodium hydroxide (8.0 mmol) was dissolved in 10 ml of ethanol and 25 ml of water and through stirring 4-[*trans*-4-n-heptylcyclohexyl]acetophenone (7.0 mmol) was added to the solution, heated to 40°C in a steam bath for 15 min, and then 7.5 mmol of aromatic aldehyde was added. The temperature of the reaction mixture was kept at about 40–50°C with continued stirring for 2 h. After cooling to room temperature, the crude product was filtered under suction and recrystallized from EtOH giving pale yellow crystals.

1-[4-(trans-4-n-heptylcyclohexyl)phenyl]-3[4-n-octoxyphenyl]-2-propen-1-one- 1A3

mp 111,0°C, yield 60%. IR(KBr), $\nu[\text{cm}^{-1}]$ 2900, 2840, 1680, 1590, 840, 729; ^1H NMR (200 MHz, CDCl_3 , TMS) δ [ppm]: 7.94 (d, 2H, $J=8.3$ Hz), (d, 1H, $J=15.6$ Hz), 7.56 (d, 2H, $J=8.7$ Hz), 7.40 (d, 1H, $J=15.6$ Hz), 7.30 (d, 2H, $J=8.3$ Hz), 6.92 (d, 2H, $J=8.7$ Hz), 3.97 (t, 2H, $J=6.5$, OCH_2-), 2.53 (tt, 1H, $\text{CH}-$), 1.82 (m, 4H, 2CH_2-), 1.28 (m, 29H, $1\text{CH}-$, 14CH_2-), 0.81–0.87 (m, 6H, 2CH_3); ^{13}C NMR (62.5 MHz, CDCl_3 , TMS) δ [ppm]: 189.97, 161.20, 153.05, 144.27, 136.30, 130.14, 128.61, 127.49, 127.04, 119.58, 114.86, 68.15, 44.75, 37.39, 37.26, 34.05, 33.45, 31.94, 31.89, 29.97, 29.53, 29.40, 29.27, 29.17, 26.99, 26.01, 22.70, 14.13.

1-[4-(trans-4-n-heptylcyclohexyl)phenyl]-3[5-n-dodecylthienyl]-2-propen-1-one- 1B4

mp 83–85°C, yield 66%. IR(KBr), $\nu[\text{cm}^{-1}]$ 2922, 2856, 1648, 1578, 850, 722; ^1H NMR (200 MHz, CDCl_3 , TMS) δ [ppm]: 7.88 (d, 2H, $J=8.1$ Hz), 7.82(d, 1H, $J=15$ Hz), 7.27 (d, 2H, $J=8.1$ Hz), 7.17 (d, 1H, $J=15$ Hz), 7.12 (d, 1H, $J=3,5$ Hz), 6.71 (d, 1H, $J=3,5$ Hz), 2.87 (t, 2H, $J=7,3$ Hz), 2.53 (tt, 1H, $\text{CH}-$), 1.04–1.87 (m, 41H), 0.80–0.86 (m, 6H, 2CH_3); ^{13}C NMR (62.5 MHz, CDCl_3 , TMS) δ [ppm]: 190.10, 153.81, 151.22, 138.86, 137.98, 136.75, 133.25, 129.19, 127.72, 126.26, 120.14, 45.41, 37.89, 34.68, 34.09, 32.57, 31.26, 30.60, 30.29, 30.17, 30.00, 29.71, 27.62, 23.35, 14.78.

General Procedure for Preparation of the 3,5-Disubstituted Isoxazoles

A mixture of 0.02 mol of enone, 0.03 mol of hydroxylamine hydrochloride, 50 ml of ethanol and three drops of pyridine was refluxed in a water bath for 2 h. The ethanol was removed by evaporation of the solution. To the cooled residue 10 ml of water was added, and the solution was cooled in an ice bath and stirred until the enone-oxime crystallized. The solid was filtered, washed with a little water and dissolved in 60% AcOH (20 ml) at 60°C. To this solution 0.02 mol of tetrakis(pyridine) cobalt(II) was added. After 1 min at 60°C, the mixture was allowed to cool to room temperature. The precipitated 3,5-diarylisoisoxazole or 3,5-arylthienylisoisoxazole was filtered with a Buchner funnel, washed with a small amount of dilute AcOH, and dried in air. The crude product was purified by two recrystallizations from hexane.

3-[4-(*trans*-4'-*n*-heptylcyclohexyl)phenyl]-5[2-(5-*n*-octoxyphenyl)]-isoxazole- 2A3

mp 107.0°C, yield 78%. IR(KBr), $\nu[\text{cm}^{-1}]$ 3124, 2954, 2920, 2848, 1616, 1568, 1506, 1390, 1256, 838, 720; ^1H NMR (200 MHz, CDCl_3 , TMS) δ [ppm]: 7.70 (d, 2H, $J=8.0$ Hz), 7.68 (d, 2H, $J=8.8$ Hz), 7.23 (d, 2H, $J=8.0$ Hz), 6.90 (d, 2H, $J=8.8$ Hz), 6.59 (s, 1H), 3.93 (t, 2H, $J=6.5$ Hz OCH_2-), 2.53 (tt, 1H, $\text{CH}-$), 1.90 (m, 33H, 16CH_2- , $1\text{CH}-$), 0.81–0.87 (m, 6H, 2CH_3). ^{13}C NMR (62.5 MHz, CDCl_3 , TMS) δ [ppm]: 170.92, 163.55, 161.35, 150.63, 128.05, 127.42, 120.91, 115.53, 96.63, 68.15, 45.24, 38.10, 37.97, 34.88, 34.21, 32.62, 30.66, 30.21, 30.08, 29.95, 29.86, 27.68, 26.69, 23.31, 23.39, 14.28.

3-[4-(*trans*-4'-*n*-heptylcyclohexyl)phenyl]-5[2-(5-*n*-dodecylthienyl)]-isoxazole- 2B4

mp 85–87°C, yield 58%. IR(KBr), $\nu[\text{cm}^{-1}]$ 2956, 2920, 2848, 1614, 1569, 1504, 1390, 1256, 838, 720; ^1H NMR (200 MHz, CDCl_3 , TMS) δ [ppm]: 7.70 (d, 2H, $J=8.2$ Hz), 7.30 (d, 1H, $J=3.6$ Hz), 7.20 (d, 2H, $J=8.2$ Hz), 6.70 (s, 1H), 2.78 (t, 2H, $J=7.0$ Hz), 2.45 (tt, 1H, $\text{CH}-$), 0.90 (m, 39H), 0.81 (m, 6H, 2CH_3); ^{13}C NMR (62.5 MHz, CDCl_3 , TMS) δ [ppm]: 166.04, 163.38, 150.64, 149.98, 127.28, 127.47, 127.38, 127.13, 125.78, 96.96, 45.18, 38.07, 37.92, 34.81, 34.15, 32.59, 32.18, 30.78, 30.64, 30.30, 30.21, 30.02, 29.72, 27.66, 23.36, 14.78.

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