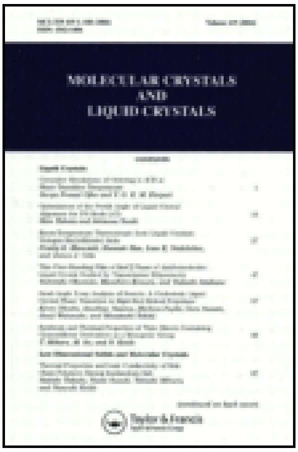


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Synthesis and Liquid Crystal Properties of Some Series Homologues of 1,2,4-Oxadiazole Derivatives

H. Gallardo [a] & I. M. Begnini [a]

[a] Departamento de Química, Universidade Federal de Santa Catarina, Cep 88000, Florianópolis, Santa Catarina, Brazil

Version of record first published: 23 Sep 2006.

To cite this article: H. Gallardo & I. M. Begnini (1995): The Synthesis and Liquid Crystal Properties of Some Series Homologues of 1,2,4-Oxadiazole Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 258:1, 85-94

To link to this article: http://dx.doi.org/10.1080/10587259508034550

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 85–94
Reprints available directly from the publisher
Photocopying permitted by license only

The Synthesis and Liquid Crystal Properties of Some Series Homologues of 1,2,4-Oxadiazole Derivatives

H. GALLARDO and I. M. BEGNINI

Departamento de Química, Universidade Federal de Santa Catarina, Cep 88000, Florianópolis, Santa Catarina, Brazil

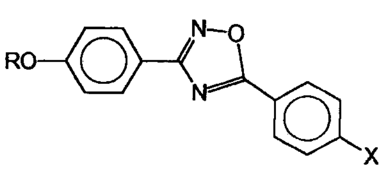
(Received September 20, 1993; in final form March 5, 1994)

Homologues series of some derivatives of 3,5-(4-substituted phenyl)-1,2,4-oxydiazole were synthesized and their phase behavior studied. Introduction of the pentagonal heteroaromatic ring leads to significant changes in mesomorphic behavior in comparison with analogous compounds containing the phenyl ring. The synthesised compounds exhibit smectic and nematic phases.

Keywords: 1,2,4-oxadiazole, nematic and smectic liquid crystals.

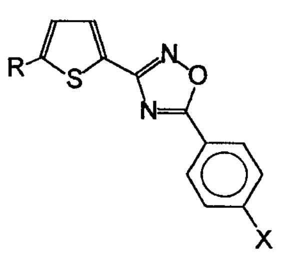
INTRODUCTION

During the last fifteen years a large number of mesomorphic compounds containing heterocyclic units have been synthesized and interest in such compounds constantly grows.[1-3] The inclusion of hetero atoms can cause large changes in the mesomorphic behavior whether in the kind of mesophase present or in the physical properties of the phases. The well-established classical concept required for mesomorphic behavior is a molecular geometry as close to linear as possible.[4] This linearity is generally obtained using the 1,4 disubstituted phenyl ring as the basic unit in the molecule. The incorpor-



$R = C_nH_{2n+1}$ $n = 5-9$

$X = -NO_2, -CN, -Br, -OR'$



$R = C_4H_9$

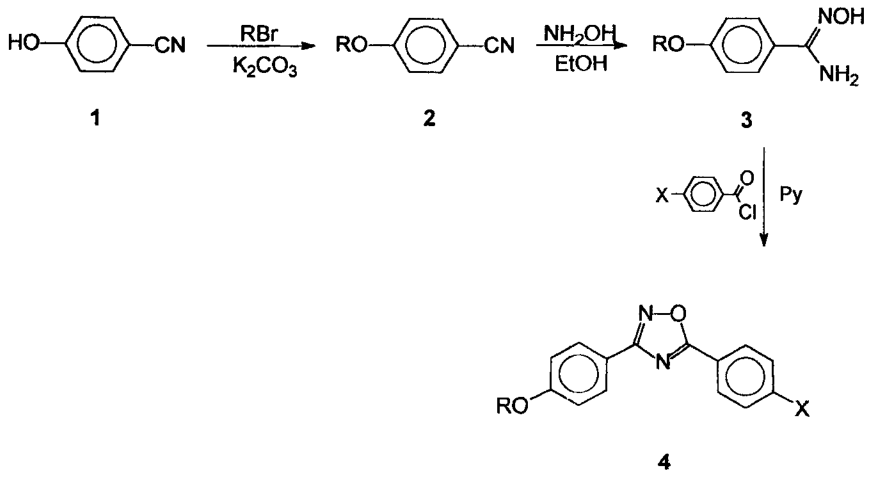
$X = -OC_{10}H_{21}, -NO_2, -CN, -Br$

ation of five member heterocyclic rings as units in the molecule has been little studied because of the low probability of generating mesophases. However, 1,3,4-thiadiazoles, 1,2,4-thiadiazoles and 1,3,4-oxadiazoles[5] pentagonal heterocyclics have been studied as structural units for liquid crystals. A disubstituted pentagonal ring is not collinear and this causes a significant loss of linearity.

Here our objective is to study the potential and compatibility of derivatives of 1,2,4-oxadiazole in the generation of mesomorphic behavior. We report the synthesis and characterization of the following compounds:

SYNTHESIS

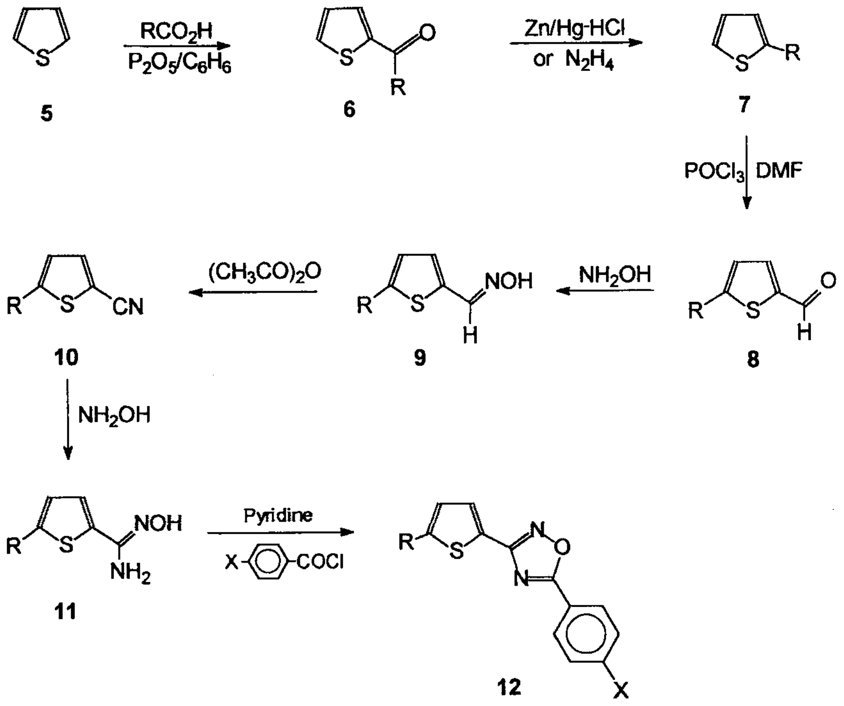
The 3,5-diaryl-1,2,4-oxadiazoles **4(a, b, c, d)** were prepared according to the synthetic route shown in scheme I. The phenolate solution obtained by the reaction of 4-hydroxybenzonitrile and potassium carbonate was treated with the appropriate bromoalkane to give the 4-alkoxybenzonitrile **2**. Compound **2** in ethanol was reacted with a solution hydroxylamine hydrochloride in water, to give the 4-*n*-alkoxybenzamidoxime **3**. The following step is the conversion of compound **3** into the 3,5-diaryl-1,2,4-oxadiazole by heating with the *p*-alkoxybenzoyl chloride or corresponding derivative of the carboxylic acids. The solvent in this reaction is pyridine which plays the role of an acceptor for HCl. The yields are good (70–75 per cent).



	R		X	
a)	C_5H_{11}-		C_nH_{2n+1}	n = 5 - 9
b)	C_nH_{2n+1}	n = 5 - 9	-NO_2	
c)	C_nH_{2n+1}	n = 5 - 9	-CN	
d)	C_nH_{2n+1}	n = 5 - 9	-Br	

SCHEME I

The reaction pathway used to prepare the 3-[2-(5-*n*-butyltienyl)]-5-(4-substituted-phenyl)-1,2,4-oxadiazoles **12(a, b, c, d)** is shown in scheme II. The acylation of the tiophene was done according to the method described in reference 6. The reduction of the compound **6** was realized either by Clemmensen reduction or Wolff–Kishner reduction. The following steps involve formylation reactions, oxime formation and dehydration with acetic anhydride. The amidoxime **11** and oxadiazoles **12(a, b, c, d)** were prepared using the same method described in scheme I.



	R	X
a)	C_4H_9-	-$OC_{10}H_{21}$
b)	C_4H_9-	-NO_2
c)	C_4H_9-	-CN
d)	C_4H_9-	-Br

SCHEME II

RESULTS AND DISCUSSION

3-(4-pentoxyphenyl)-5-(alkoxyphenyl)-1,2,4-oxadiazole. Table I summarizes the mesomorphic behavior of the serie **4a** with various chain lengths.

As can be observed in Table I, the melting point decreases slightly with increase in the chain length. The number of carbon atoms in the aliphatic chain in this serie doesn't

TABLE I

Transition Temperatures and Transition Enthalpies (kJ mol^{-1}) for the Serie of 3-(4-pentoxyphenyl)-5-(4-alkoxyphenyl)-1,2,4-oxadiazoles, (**4a**)

n		K		S_A		N	I
5	·	106.2 [52.4]	–		·	(101.0) [0.5]	·
6	·	92.7 [46.7]	–		·	102.0 [1.6]	·
7	·	88.8 [46.6]	–		·	100.4 [1.7]	·
8	·	89.2 [57.6]	–		·	103.7 [1.6]	·
9	·	98.6 [47.0]	–		·	102.9 [1.8]	·
10	·	97.0 [44.4]	·	(89.1)*	·	103.0 [1.7]	·

* Monotropic transitions in parentheses

affect significantly the mesomorphic behavior of the mesogens. An enantiotropic nematic mesophase is dominant for homologues with $n = 6, 7, 8, 9$ and 10, while the homologue $n = 5$ shows a monotropic nematic mesophase. The nematic isotropic transition temperature shows the usual odd-even alternation as the aliphatic chain length increases. A smectic A phase is present only as a monotropic mesophase in the longest chain derivative, $n = 10$. Solid–solid transitions were not observed in this serie of mesogens.

The nematic mesophases for all compounds, in this serie, exhibit schlieren textures and the typical nematic droplets are observed on cooling from the isotropic liquid. The monotropic smectic phase observed at 89.1°C appears to be smectic A. The phase separates on cooling the nematic phase in the form of batonnets and these batonnets coalesce to form a focal-conic fan texture; there is a strong tendency to assume a homeotropic texture.

The serie 3-(4-*n*-pentoxyphenyl)-5-(4-*n*-alkoxyphenyl)-1,2,4-oxadiazole **4a** shows a considerably lower thermal stability of the nematic phase than purely heteroaromatic compounds having similar molecular structures such as 2-[4-*n*-alkylphenyl]-5-[4-*n*-alkoxyphenyl]pyrimidine.[7] Also, the pyrimidine derivatives show a rich smectic polymorphism, for example, the homologue with $n = 5$ and $m = 5$ shows K 79.5 S_H (61.5) S_G 102.4 S_F 113.2 S_C 144.8 S_A 210 I, whereas serie **4a** shows only a monotropic smectic A for $n = 10$.

Probably, the low thermal stability of the serie 3-(4-*n*-pentoxyphenyl)-5-(4-*n*-alkoxyphenyl)-1,2,4-oxadiazole is due to the presence of the pentagonal heterocyclic ring which produces a non-linear substitution and thereby a molecular curvature that inhibits the formation of mesophases. In the majority of known liquid crystal compounds there is colinear 1,4-disubstitution of the benzene ring whereas derivatives of 3,5-disubstituted-1,2,4-oxadiazole are clearly not very linear. This effect seems to be especially accentuated with an increase in the aliphatic chain length because when the

TABLE II

Transition Temperatures and Transition Enthalpies (kJ mol^{-1}) for the Serie of 3-(4-alkoxyphenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazoles, (**4b**)

n	*K*		S_A		*N*		*I*
5	·	154.0 [60.2]	·	(148.4)*	·	(148.9)	·
6	·	116.3 [27.4]	·	158.00 [8.9]	–		·
7	·	124.4 [66.8]	·	154.2 [7.6]	–		·
8	·	123.8 [35.5]	·	161.9 [9.8]	–		·
9	·	121.7 [30.6]	·	154.8 [13.2]	–	102.9	·

* Monotropic transitions in parentheses

terminal alkoxy group is replaced by a small compact group such as nitro or cyan the thermal stability increases, (e.g., Table II, III).

3-(4-*n*-alkoxyphenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole. The transition temperature and enthalpies for the serie **4b**, are given in Table II. The melting point decreases slightly with increase in the chain length. The enthalpies of fusion and of the smectic A-isotropic transition can be considered normal.

The first compound with $n = 5$ shows monotropic smectic A and nematic phases. The other homologues show an enantiotropic smetic A phase and exhibit the normal pattern of alternation with temperature.

The texture observed with the polarizing microscope for the smectic S_A phase was focal-conic or homeotropic. The homeotropic texture observed in convergent light shows a centered uniaxial positive cross. The presence of the smectic A phase in this serie can be explained in terms of non-linear geometry and conjugate effects. The lone pair of the oxygen in the heterocyclic ring may conjugate with the nitro group through the aromatic group and thereby set-up a permanent dipole, which has a substantial component directed laterally. This would increase the lateral intermolecular cohesive forces and the tendency to form a smectic mesophase.

3-(4-*n*-alkoxyphenyl)-5-(4-cyanophenyl)-1,2,4-oxadiazole. The liquid crystal transition temperatures and corresponding enthalpy changes for the serie, **4c**, are listed in Table III.

On cooling from the isotropic liquid, the early homologues, $n = 5$ and $n = 6$, give rise only to a monotropic nematic phase. For $n = 7$ an enantiotropic nematic phase appears and for $n = 8$ and $n = 9$ there are enantiotropic smectic A and nematic phases. The nematic mesophase for all compound in this serie exhibits schlieren textures and the typical nematic droplets are observed on cooling from the isotropic liquid. The smectic phase separates on cooling the nematic phase in batonnets that form well-defined focal-conic fans interspersed with homeotropic areas, typical of a S_A phase; there is a strong tendency to assume a homeotropic texture on shearing the cover glass.

3-(4-*n*-alkoxyphenyl)-5-(4-bromophenyl)-1,2,4-oxadiazole. The transition temperatures and the associated enthalpy changes for the serie **4d**, are presented in Table IV.

TABLE III

Transition Temperatures and Transition Enthalpies (kJ mol^{-1}) for the Serie of 3-(4-*n*-alkoxyphenyl)-5-(4-cyanophenyl)-1,2,4-oxadiazoles, (**4c**)

n	*K*	S_A	*N*	*I*
5	· 159.0 [55.5]	–	· (153.8)*	·
6	· 148.4 [48.3]	–	· (145.5)	·
7	· 138.1 [44.9]	–	· 145.0	·
8	· 135.5 [45.9]	· 136.3	· 147.9	·
9	· 130.0 [42.4]	· 145.1	· 147.3	·

* Monotropic transitions in parentheses

TABLE IV

Transition Temperatures and Transition Enthalpies (kJ mol^{-1}) for the Serie of 3-(4-*n*-alkoxyphenyl)-5-(4-bromophenyl)-1,2,4-oxadiazoles, (**4d**)

n	*K*	S_A	*N*	*I*
5	· 148.8 [49.5]	–	–	·
6	· 106.4 [42.5]	–	· (95.2)*	·
7	· 99.2 [37.1]	–	· (90.8)	·
8	· 90.0 [37.9]	– (86.6)	· 98.9	·
9	· 102.9 [36.4]	–	· (94.0)	·

* Monotropic transitions in parentheses

The first compound with $n = 5$ is not a liquid crystal and the other homologues with $n = 6, 7$ and 9 show only a monotropic nematic phase. The homologue with $n = 8$ shows a monotropic smectic A and enantiotropic nematic phase.

The mesophases were classified on the basis of the microscopic examination; namely, the nematic phase by a schlieren texture, the smectic A phases by fan texture. The smectic A phase appearing on cooling of the nematic phase tends to be homeotropic. This series shows a considerably lower thermal stability of the nematic and smectic phases. This may be due to a substantial decrease in the polarization that would result because there is no conjugation between the heteroatom of the heterocyclic ring and the terminal bromo group.

3-[2-(5-*n*-alkyltienyl)]-5-(4-subtitutedphenyl)-1,2,4-oxadiazole. The transition temperatures for the compounds **12(a, b, c, d)** are shown in Table V. The molecular geometry of these compounds does not favor, at all, the occurrence of mesomorphic behavior. The molecule is even more non linear than 3,5-diaryl-1,2,4-oxadiazole

TABLE V

Transition Temperatures of the Compounds **12a, b, c, d**

Compound	K	S_A	N	I
12a	· 103.4	–	–	·
12b	· 77.9	· 88.9	–	·
12c	· 105.7	–	· (98.9)*	·
12d	· 87.5	–	–	·

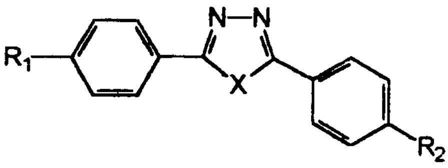
* Monotropic transitions in parentheses

compound. Indeed, the compound with a $n = 10$ alkoxy terminal group (**12a**) and bromo terminal group (**12d**) does not show mesomorphic behavior. However, compound (**12b**) with a terminal nitro group and (**12c**) with a terminal cyan group do show mesophases. With the nitro terminal group a enantiotropic S_A phase is observed and with the cyan group a monotropic nematic phase. These two compounds are strong candidates for the generation of mesophases at lower temperatures than observed here. Since the terminal alkyl group has only four carbons, an increase in the number of carbons of the alkyl group should stabilize their mesophases.

Tables I and IV should be compared with Table VI which shows the mesogenic properties of some derivatives of 1,3,4-thiadiazole and 1,3,4-oxadiazole from the work

TABLE VI

Transition Temperatures for the Compounds Derivatives of the 1,3,4-thiadiazoles and 1,3,4-oxadiazoles[5]



X	R_1	R_2	K	Sc	Sa	N	I
S	$C_6H_{13}O$	$C_6H_{13}O$	· 109	–	· 184	· 204	·
O	$C_6H_{13}O$	$C_6H_{13}O$	· 121	–	–	–	·
S	$C_5H_{11}O$	CN	· 142	–	· 246	– 265	·
S	$C_6H_{13}O$	CN	· 146	–	· 258	· 264	·
O	$C_6H_{13}O$	CN	· 160	–	–	–	·
S	$C_5H_{11}O$	$C_5H_{11}O$	· 119	–	· 173	· 205	·
S	$C_6H_{13}O$	$C_6H_{13}O$	· 109	–	· 184	· 024	·
S	$C_7H_{15}O$	$C_7H_{15}O$	· 92	· 183	–	· 193	·
S	$C_8H_{17}O$	$C_8H_{17}O$	· 99	· 195	–	–	·
S	$C_9H_{19}O$	$C_9H_{19}O$	· 93	· 187	–	–	·
S	$C_6H_{13}O$	Br	· 135	–	· 239	–	·
S	$C_6H_{13}O$	NO_2	· 123	–	· 241	–	·

of Zaschke, *et al.* (5). All compounds that have a 1,3,4-thiadiazole ring show enantiotropic phases over intervals of about 100°C. However, compounds with a 1,3,4-oxadiazole ring are not mesomorphic and this behavior is related to the larger molecular curvature caused by the 1,3,4-oxadiazole ring. For the derivatives with a 1,2,4-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 produzed by disubstitution of these heterocyclic rings.

EXPERIMENTAL

The transition temperatures for all compounds were determined by optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Metter FP-52 heating stage. The transition temperatures and enthalpies were also determined from DSC measurements using a Perkin–Elmer DSC-2. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard. The purity of the compounds was evaluated by thin layer chromatography and elemental analysis. The IR spectra were recorded using KBr disc with a Perkin–Elmer model 283 spectrometer, and the ^{1}H NMR and ^{13}C NMR spectra were recorded at 80 MHz (Bruker WP-80) or 270 MHz (Bruker HX-270).

The *p*-alkoxybenzoyl chlorides were either obtained commercially or prepared by standard methods.

4-*n*-Alkoxybenzonitril (2). A mixture of *p*-cyanophenol (0.419 mole), potassium carbonate (0.419 mole) and dry cyclohexanone (50 ml) was heated at 65°C for several minutes. Then alkyl bromide (0.429 mole) was added dropwise and the reaction mixture refluxed for 24 h. After filtration and evaporation of the solvent the oil residue was purified by destillation under reduced pressure. Yield and b.p.: 87 per cent for $R = C_5$, 132°C/0.6 (mm Hg); 70 per cent for C_6, 138°C/0.5 (mm Hg); 73 per cent for C_7, 140°C/0.3 (mm Hg); 70 per cent for C_8, 156°C/0.3 (mm Hg); 65 per cent for C_9, 164°C/0.3 (mm Hg). **IR** (film)ν_{max}: 2930, 2850, 2210, 1600, 1450, 1250, 1160, 830 cm^{-1}. Elemental analysis results (CHN) were satisfactory.

4-*n*-Alkoxybenzamidoxime (3). To a solution of (0.178 mole) hydroxylamine hydrochloride in a mixute of (0.178 mole) of sodium hydroxide in 10 ml of water was added a solution of the (0.158 mole) of 4-*n*-Alkoxybenzonitrile in 80 ml of ethanol. The mixture was heated under reflux of 3 h. After the mixture was cooled in an ice bath for 2 h, colorless crystals were collected for filtration and dried. The crystals were recrystallized from ethanol or a mixture ethanol/water. The yields for all compounds were in the range 70–77 per cent. **IR** (KBr)ν_{max}: 3430, 3330, 3170, 2930, 2850, 1640, 1600, 1510, 1250, 830 cm^{-1}. Elemental analysis results (CHN) were satisfactory.

3,5-Diaryl-1,2,4-oxadiazoles (4). General method: 4-*n*-alkoxy-benzamidoxime (4.5 mmole) was dissolved in dry pyridine (15 ml). The apropriate *p*-*x*-benzoyl chloride (4.7 mmole) was then added drop wise. The mixture was heated under reflux for 5 h. The cooled reaction mixture was poured into water (100 ml). The crude product was purified by several recrystallization from ethanol or the mixture ethanol/benzene. Elemental analysis results (CHN) were satisfactory.

Data for **3-(4-pentyloxyphenyl)-5-(4-*n*-octyloxyphenyl)-1,2,4-oxadiazole, IR** (KBr) ν_{max}: 2920, 2840, 1600, 1560, 1240, 1170, 905, 840 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80-MHz): $\delta = 8.40$ (d, BB′ part of an AA′BB′, $J = 8.3$ Hz, 2 H), 8.36 (d, BB′ part of an AA′BB′, $J = 8.3$ Hz, 2 H), 7.23 (m, AA′ part of an AA′BB′, $J = 8.3$ Hz, 4 H), 4.17 (t, overlapping peaks, $J = 6.2$ Hz, 4 H, —OCH_2—), 2.18 – 1.17 (m, 18 H, —CH_2—), 0.97 (t, overlapping peaks, 6 H, CH_3). Elemental analysis results (CHN) were satisfactory.

Data for **3-(4-*n*-heptyloxyphenyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole, IR** (KBr) ν_{max}: 2910, 2840, 1600, 1580, 1525, 1250, 920, 845, 740 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.63$ (s, 4 H), 8.34 (d, $J = 9.3$ Hz, 2 H), 7.23 (d, $J = 9.3$ Hz, 2 H), 4.16 (t, $J = 6.2$ Hz, 2 H, OCH_2), 2.25–1.10 (m, 10 H, —CH_2), 0.92 (t, 3 H, —CH_3). Elemental analysis results (CHN) were satisfactory.

Data for **3-(4-*n*-nonyloxyphenyl)-5-(4-cyanophenyl)-1,2,4-oxadiazole, IR** (KBr) ν_{max}: 2920, 2840, 2220, 1580, 1545, 1460, 1240, 905, 830 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.27$ (d, $J = 8.8$ Hz, 2 H), 8.03 (d, $J = 8.8$ Hz, 2 H), 7.79 (d, $J = 8.8$ Hz, 2 H), 6.96 (t, $J = 8.8$ Hz, 2 H), 4.16 (t, $J = 6.4$ Hz, 2 H, —OCH_2), 1.80 – 1.30 (m, 14 H, —CH_2), 0.88 (t, $J = 6.4$ Hz, 3 H). Elemental analysis results (CHN) were satisfactory.

Data for **3-(4-*n*-octyloxphenyl)-5-(4-bromophenyl)-1,2,4-oxadiazole, IR** (KBr) ν_{max}: 2910, 2840, 1600, 1545, 1450, 1245, 915, 830, 650 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.30$ (d, $J = 9.3$ Hz, 4 H), 7.88 (d, $J = 9.3$ Hz, 2 H), 7.20 (d, $J = 9.3$ Hz, 2 H), 4.13 (t, $J = 6.2$ Hz, 2 H, —OCH_2—), 1.93 – 1.14 (m, 12 H, —CH_2), 0.92 (t, 3 H, —CH_3). Elemental analysis results (CHN) were satisfactory.

3-(5-*n*-butyl-2-thienyl)-5-(4-substituted-phenyl)-1,2,4-oxadiazole, 12(a, b, c, d) were prepared as described previously for the 3,5-diaryl-1,2,4-oxadiazoles. The intermediates compound in the synthetic scheme were prepared as described in reference 6.

3-(5-*n*-Butyl-2-thienyl)-5-(4-*n*-decyloxyphenyl)-1,2,4-oxadiazole (12a), m.p. 103.5–104.5°C. **IR** (KBr) ν_{max} 2900, 2830, 1600, 1565, 1245, 905 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.40$ (d, $J = 9.3$ Hz, 2 H), 7.95 (d, $J = 4.1$ Hz, 1 H), 7.23 (d, $J =$ 9.3 Hz, 2 H), 7.08 (d, $J = 4.1$ Hz, 1 H), 4.15 (t, $J = 6.2$ Hz, 2 H), 2.95 (t, $J = 6.2$ Hz, 2 H), 2.0 – 1.13 (m, 4 H), 0.90 (t, 3 H).

3-(5-*n*-Butyl-2-thienyl)-5-(4-nitrophenyl)-1,2,4-oxadiazole (12b), K 77.9 S_A 88.9 I. **IR** (KBr) ν_{max}: 2910, 2825, 1610, 1565, 1520, 1340, 900, 850, 810, 735 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.28$ (s, 4 H), 7.60 (d, $J = 4.1$ Hz, 1 H), 6.80 (d, $J = 4.1$ Hz, 1 H), 2.87 (t, $J = 6.2$ Hz, 2 H), 2.10 – 1.20 (m, 4 H), 0.97 (t, 3 H).

3-(4-*n*-Butyl-2-thienyl)-5-(4-cyanophenyl)-1,2,4-oxadiazole (12c), K 105.7 N (98.9) I. **IR** (KBr) ν_{max}: 2960, 2890, 2260, 1600, 1585, 1510 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.53$ (d, $J = 9.3$ Hz, 2 H), 8.07 (d, $J = 9.3$ Hz, 2H), 7.90 (d, $J = 4.1$ Hz, 1 H), 7.07 (d, $J = 4.1$ Hz, 1 H), 3.0 (t, $J = 6.2$ Hz, 2 H), 2.10–1.30 (m, 4 H), 0.97 (t, 3 H)

3-(4-*n*-Butyl-2-thienyl)-5-(4-bromophenyl)-1,2,4-oxadiazole (12d), m.p. 87–88°C. **IR** (KBr) ν_{max}: 2910, 2820, 1600, 1570, 1500, 1360, 915, 840, 800, 750 cm^{-1}. ^{1}**H NMR** ($CDCl_3$, TMS, 80 MHz): $\delta = 8.03$ (d, $J = 9.3$ Hz, 2 H), 7.65 (d, $J = 4.1$ Hz, 1 H), 7.63 (d, $J = 9.3$ Hz, 2 H), 6.82 (d, $J = 4.1$ Hz, 1 H), 2.88 (t, $J = 6.2$ Hz, 2 H), 1.90 – 1.20 (m, 4 H), 0.96 (t, 3 H).

Acknowledgement

The authors gratefully acknowledge the financial support of FUNCITEC and CNP_q.

References

1. W. M. Deutscher, H. M. Vorbradt and H. Zaschke, *Z., Chem.*, **21**, 9 (1981).
2. R. Cai and E. T. Samulski, *Liq. Crystals*, **9**, 617 (1991).
3. D. Girdziunaite, C. Tschierske, E. Novotna, H. Kresse and A. Hetzheim, *Liq. Crystals*, **10**, 397 (1991).
4. D. Demus, *Liq. Crystals*, **5**, 75 (1989).
5. K. Dimitrowa, J. Hauschild, H. Zaschke and H. Schubert, *J. Prakt. Chem.*, **322**, 933 (1980).
6. H. Gallardo and I. Favarin, *Liq. Crystals*, **13**, 115 (1993).
7. D. Demus and H. Zaschke, *Flüssige Kristalle in Tabellen* (VED Deutscher Verlag für Grundstoffindustrie, Leipzig), 1984.