Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

New supramolecular liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and 2,5-thiophene dicarboxylic acid

M. Parra[a]; P. Hidalgo[a]; J. Alderete[a]
[a] Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Casilla 160-C, Concepción, Chile

To cite this Article Parra, M. , Hidalgo, P. and Alderete, J.(2005) 'New supramolecular liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and 2,5-thiophene dicarboxylic acid', Liquid Crystals, 32: 4, 449 — 455
To link to this Article: DOI: 10.1080/02678290500075142
URL: http://dx.doi.org/10.1080/02678290500075142

Liquid Crystals, Vol. 32, No. 4, April 2005, 449–455

Taylor & Francis
Taylor & Francis Group

New supramolecular liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and 2,5-thiophene dicarboxylic acid

M. PARRA*, P. HIDALGO and J. ALDERETE

Facultad de Ciencias Químicas, Departamento de Química Orgánica, Universidad de Concepción, Casilla 160-C, Concepción, Chile

(*Received 30 September 2004; in final form 10 December 2004; accepted 13 December 2004*)

Supramolecular liquid crystalline complexes were obtained from binary mixtures of 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles and 2,5-thiophene dicarboxylic acid. Although the oxadiazole derivatives and the dicarboxylic acid are non-mesomorphic, the H-bonded complexes exhibit mesomorphism. Their liquid crystalline properties were investigated by differential scanning calorimetry and polarizing optical microscopy. The complexes exhibit enantiotropic nematic phases. A structural study involving AM1 semi-empirical calculations is also described.

1. Introduction

The self-assembly of aromatic carboxylic acids as proton donors with pyridyl fragments as proton acceptors is most frequently used in the formation of H-bonded structures. Hydrogen bonding leads to an elongation of the rigid rod segment of the individual components, and in this manner the simplest H-bonded complexes possessing mesogenic properties are obtained. Most published work is summarized in three review papers [1–3]; examples of more recent papers are quoted in references [4–11].

Compounds containing five-membered heteroaromatic rings, such as thiadiazole or oxadiazole, may be incorporated into the principal structure of calamitic mesogens to give desired properties. The introduction of heterocycles within the central core of calamitic molecules strongly influences their mesomorphic behaviour due, in part, to the dipolar moment associated with the heterocyclic ring [12]. Recently, we reported the first example of pyridine derivatives containing the thiadiazole ring in their structure [10]. These compounds were used as proton acceptors in the formation of mesomorphic H-bonded complexes with 4-*n*-nonyloxybenzoic acid as proton donor. In this case both the proton acceptor and proton donor are themselves mesogenic, and the hydrogen bonding plays an important role in the stabilization of the mesophases exhibited by the individual components. However, liquid crystals induced by intermolecular hydrogen bonding using proton donor or proton acceptor molecules containing the oxadiazole unit in their structure, to our knowledge, have never been reported.

The aim of this work was to obtain new supramolecular liquid crystals induced by intermolecular hydrogen bonding by using 3-(4-pyridyl)-5-(4-*n*-alkoxy)phenyl-1,2,4-oxadiazoles (series **2a**–**e**) as the proton acceptors, and 2,5-thiophene dicarboxylic acid as the proton donors, and to study their mesomorphic properties by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The results show that all of these complexes are nematic liquid crystals. It is interesting to note that both the oxadiazole derivatives (series **2a**–**e**) and the dicarboxylic acid are themselves non-mesomorphic, therefore the hydrogen bonding is responsible for the formation of liquid crystals in binary mixtures.

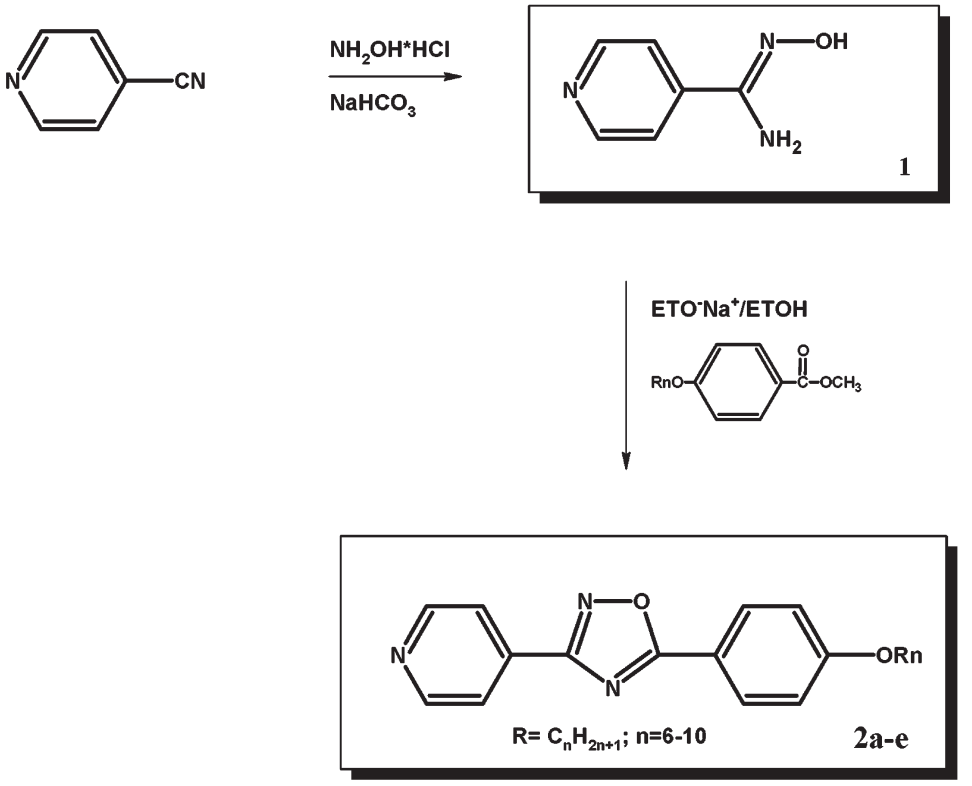
2. Results and discussion

2.1. *Synthesis*

The synthesis of the compounds is outlined in the scheme. The 1,2,4-oxadiazole derivatives **2a**–**e** were synthesized starting with the condensation of 4-cyanopyridine and hydroxylamine hydrochloride yielding the corresponding amidoxime **1**. This was reacted with methyl 4-*n*-alkoxybenzoate (n=6–10) in an ethanolic

*Corresponding author. Email: mparra@udec.cl

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis Group Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500075142



Scheme. Synthetic route for oxadiazoles of series **2a**–**e**.

solution of sodium ethoxide leading to the formation of the 1,2,4-oxadiazoles **2a**–**e** [13].

Torgova *et al*. reported mesogenic pyridyl-1,2,4-ozadiazole analogous (see figure 1) [14]; in contrast to this, the oxadiazoles synthesized by us (**2a**–**e**) are not mesogenic. This can be attributed to the greater molecular length of the alkylcyclohexane present in the molecule synthesized by Torgova *et al*. Their interest in these compounds was to study the correlation between mesomorphic properties and the position of the nitrogen atom in the pyridine ring, for this reason these authors also synthezised the 2- and 3-pyridyl-1,2,4-oxadiazoles analogues.

2.2. *Hydrogen-bonded complexes and their thermal and phase behaviour*

The H-bonded complexes, series **3a**–**e**, were prepared using 2,5-thiophene dicarboxylic acid as proton donor and the 1,2,4-oxadiazole derivatives **2a**–**e** as proton acceptors in 1:2 molar ratio. The five-membered heterocyclic (oxadiazole) supplies an extra dipole and the pyridine ring serves as the binding site of the hydrogen bonds. Figure 2 shows a representation of the H-bonded complexes.

Examination by DSC and POM revealed that all the H-bonded complexes in the series **3a**–**e** show mesomorphic properties. In each case an enantiotropic

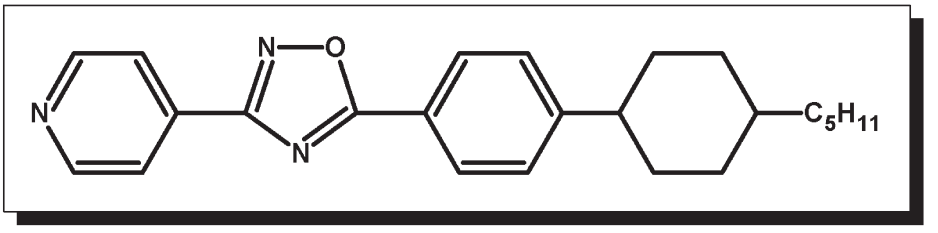


Figure 1. Structure of oxadiazole analogue synthesized by Torgova *et al*. (Cr 74.7 Sm 80 N 157 I) [14].

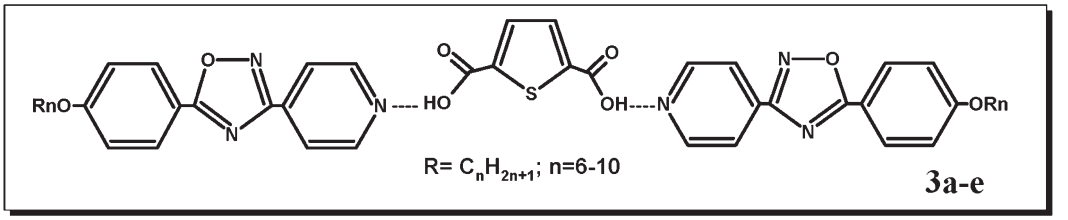


Figure 2. Representation of the hydrogen-bonded complexes of series **3a**–**e**.

nematic mesophase is observed, showing an odd–even alternation effect for the nematic to isotropic transition. Melting and clearing temperatures decrease with increase in chain length. The first member of the series (n=6) has a smaller mesophase range (2°C), while the other homologues (n=7–10) have broader mesomorphic range.

Neither the proton donor (2,5-thiophene dicarboxylic acid) nor proton acceptors (**2a**–**e**) show liquid crystals properties alone, therefore the hydrogen bonding is responsible for the formation of mesophases. Optical, thermal and thermodynamic data for the H-bonded complexes **3a**–**e** are gathered in the table 1; a graphical representation of the mesomorphic behaviour is presented in figure 3.

Lin *et al.* [15] reported non-linear mesogenic hydrogen-bonded complexes formed by mixing either *trans*-4-alkoxy-4′-stilbazoles or 4-alkoxypyridines with 2,5-thiophene dicarboxylic acid. The main difference between these complexes and the H-bonded complexes **3a**–**e** is in their proton acceptor moieties. The former have two or one aromatic ring, (pyridine and benzene rings in the stilbazole derivatives and a pyridine ring in the alkoxypyridine derivatives), whereas the latter have three aromatic rings (pyridine, oxadiazole and benzene rings). The complexes reported by Lin have a broader mesomorphic range than the complexes **3a**–**e** and display smectic and nematic phases. The nematic phase is favoured by shorter flexible chain lengths and its temperature range decreases as the alkoxy chain lengths increase. In contrast to this, the H-bonded complexes **3a**–**e**, show only a nematic phase which is favoured by longer flexible chain lengths, and its temperature range increases as the alkoxy chain lengths increase.

Table. Transition temperatures and enthalpy changes for the hydrogen-bonded complexes of series **3a**–**e**: Cr=crystal, N=nematic, I=isotropic.

Complex	Transition	Temperature/ °C	ΔH/J g^{-1}
3a (n=6)	Cr–N	175.0	55.6
	N–I	177.0	2.3
	I–N	170.5	2.4
	N–Cr	157.1	54.3
3b (n=7)	Cr–N	159.7	33.7
	N–I	173.2	2.1
	I–N	162.9	2.0
	N–Cr	142.0	34.7
3c (n=8)	Cr–N	146.2	46.9
	N–I	166.8	2.8
	I–N	157.9	2.0
	N–Cr	134.6	45.5
3d (n=9)	Cr–N	134.1	27.0
	N–I	150.4	3.0
	I–N	145.1	2.5
	N–Cr	116.7	33.5
3e (n=10)	Cr–N	126.2	24.2
	N–I	147.6	1.9
	I–N	136.0	2.2
	N–Cr	117.6	28.9

2.3. *Textures observed by polarizing optical microscopy*

The mesophases exhibited by H-bonded complexes **3a**–**e** were identified from their optical textures observed by POM during heating and cooling. Phase transition temperatures observed through thermal microscopy were found to be in reasonable agreement with the corresponding DSC thermograms. The nematic phase showed the typical schlieren texture with characteristic two- and four-brush singularities and typical nematic droplets (see figure 4).

2.4. *Phase diagram*

In order to obtain stoichometric information on the binary mixtures, a series of H-bonded complexes was prepared using a varying mol% of **2d** (n=9) as proton acceptor, and 2,5-thiophene dicarboxylic acid as proton donor. The phase diagram is given in figure 5. The liquid crystal behaviour of the binary mixtures was studied by DSC and POM.

In the binary mixtures the melting point occurs at a temperature lower than the melting point of pure thiophene acid and higher than that of pure **2d**. Binary mixtures with 10 and 90 mol% of **2d** show no mesomorphic behaviour, while binary mixtures with 10 to 80 mol% of **2d** show an enantiotropic nematic phase. The binary mixture with 66 mol% of **2d** shows the highest clearing point and broadest mesophase stability,

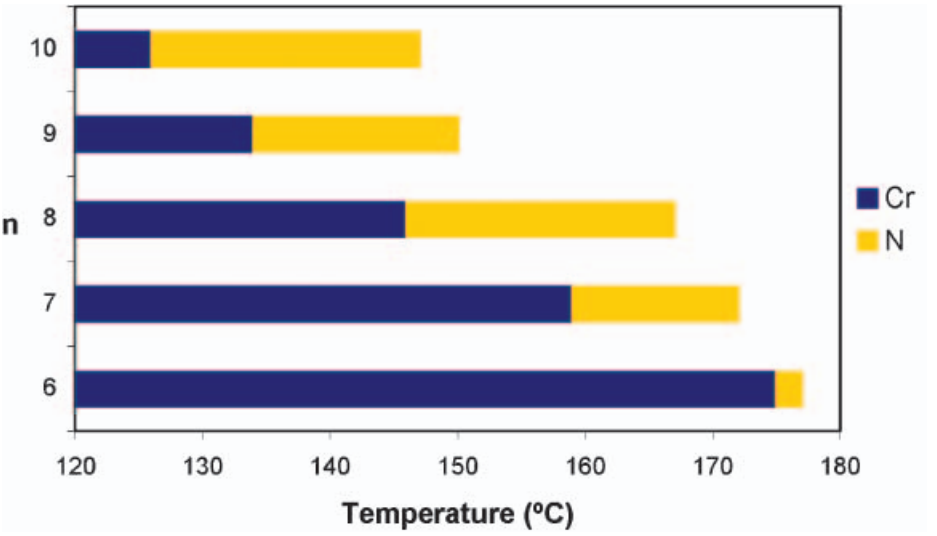
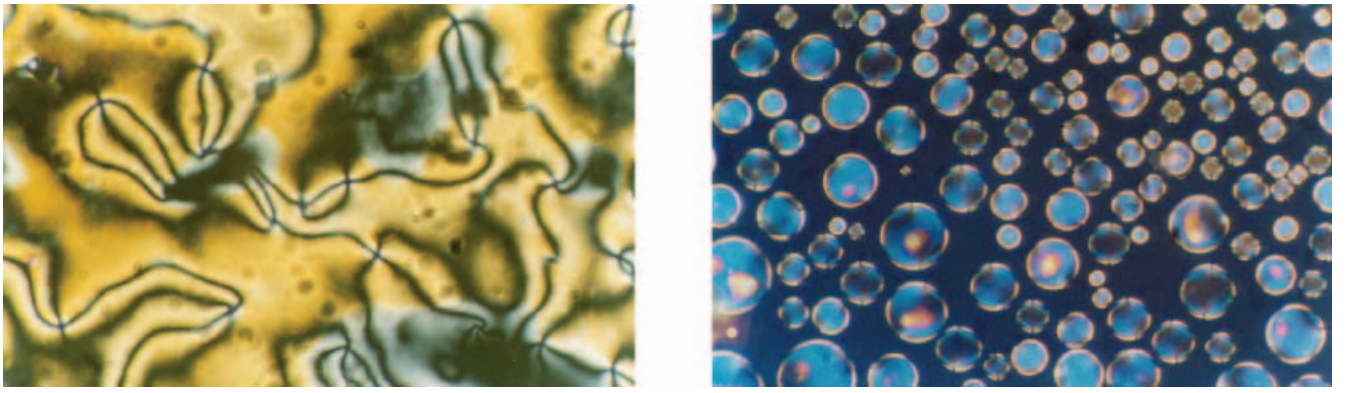


Figure 3. Plot of transition temperatures versus the number of carbon atoms in the alkoxy chain for the hydrogen-bonded complexes of series **3a**–**e**.



(*a*) (*b*)

Figure 4. Mesophase textures obtained by cooling. (*a*) Schlieren texture at 145°C of complex **3c**; (*b*) nematic droplets at 156°C of complex **3c**.

suggesting that the interactions between **2d** and thiophene dicarboxylic acid are particularly strong. This indicates that a well defined 1:2 stoichiometric complex is formed, resulting from the hydrogen bonding of one thiophene dicarboxylic acid molecule to two **2d** molecules.

2.5. *FTIR spectroscopy*

Infrared spectroscopy was used to identify hydrogen bonding in the complexes of series **3a**–**e**. The spectrum of 2,5-thiophene dicarboxylic acid shows a sharp band at 1663 cm^{-1} corresponding to a carbonyl band. Furthermore, a very broad and strong OH band centred at 3000 cm^{-1}, along with two bands at 2650 and 2540 cm^{-1}, which are considered to be Fermi resonances, are observed [16–19]. The carbonyl band at 1663 cm^{-1} and the characteristic bands of the pure dicarboxylic acid at 2650, 2540 and 3000 cm^{-1}, disappear completely in the complexes.

The carbonyl band at 1663 cm^{-1}, corresponding to pure thiophene dicarboxylic acid, is replaced by the carbonyl band at ~1680 cm^{-1}, suggesting the formation of the H-bonded complex between the pyridine ring and OH groups of the dicarboxylic acid. In the complexes this band is the unique carbonyl band. These results suggest that the thiophene dicarboxylic acid is engaged entirely in the formation of stoichiometric 1:2 complexes.

On the other hand, two additional broad bands at around 1900 and 2500 cm^{-1} appear in the spectra of the complexes, indicating that strong hydrogen bonding takes place between the pyridine ring of the oxadiazole derivatives (series **2a**–**e**) and the carboxylic groups of the thiophene dicarboxylic acid [20–22].

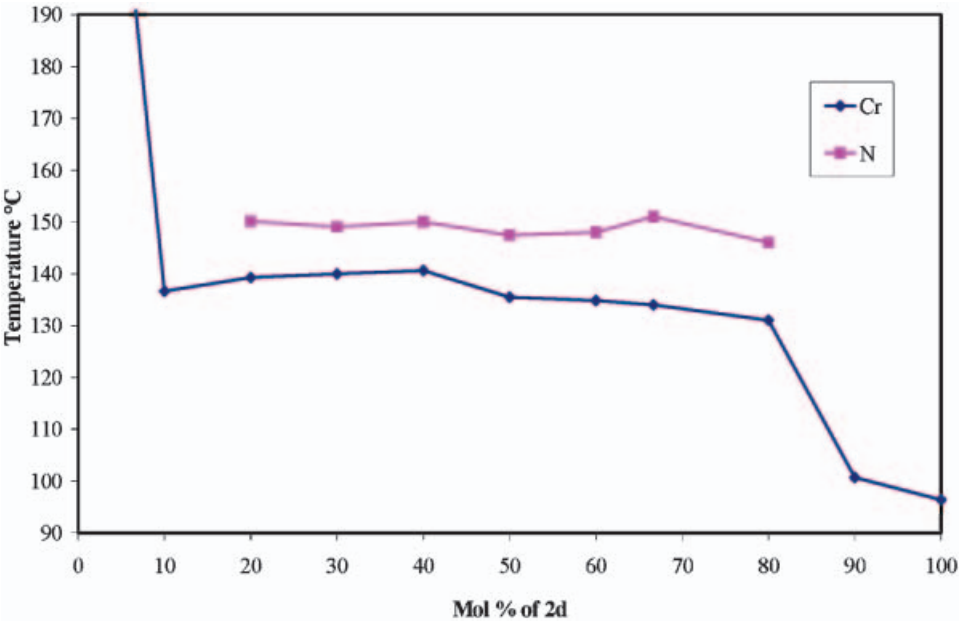


Figure 5. Phase diagram of the binary mixture of **2d** (m.p. 96°C) with 2,5-thiophene dicarboxylic acid (m.p. >300°C): Cr=crystal, N=nematic.

2.6. *Semi-empirical calculations*

In order to obtain structural information we performed semi-empirical calculations at AM1 level, implemented on the GAUSSIAN 94 W series of programs [23, 24]. We used the derivative with a methoxy terminal chain as molecular model. Several initial conformations were optimized, for the H-bonded series **3** complexes. In general, no difference of energy was found between the different conformations generated from the relative dispositions of the 1,2,4-oxadiazole ring and carboxylic groups.

Figure 6 shows the two extreme conformations. The linearity of the complexes is affected by the relative orientation of the carboxylic groups. Thus the conformation with the carbonyl group *anti* with respect to the central thiophene ring is not linear, figure 6 (*a*). The other conformation with the carbonyl group *syn* with respect to the central thiophene ring has a non-linear boomerang shape, figure 6 (*b*). From these studies we conclude that the geometry of figure 6 (*b*) is the most favoured, and would give rise to the best molecular packing for the formation of a mesophase.

3. Experimental

3.1. *Characterization*

The structures of the compounds were confirmed by ^{1}H NMR, ^{13}C NMR (Bruker AC-250P) and FTIR (Nicolet 550) spectra. The purity of the final products was evaluated by thin layer chromatography.

Transition temperatures and mesophase textures were determined by optical microscopy using an Ortholux Pol BK-11 polarizing microscope equipped with a Mettler FP 800 hot stage. Transition temperatures and enthalpy changes were investigated by DSC using a Rheometric DSC-V calorimeter. Samples were encapsulated in aluminium pans and studied at a scanning rate of 5°C min^{-1} during heating and cooling. The instrument was calibrated using an indium standard (156.6°C, 28.44 J g^{-1}).

3.2. *Synthesis*

3.2.1. 4-Pyridylamidoxime (1) [13]. Sodium bicarbonate (70 mmol, 5.88 g) was added in portions to a solution of hydroxylamine hydrochloride (70 mmol, 4.79 g) in 18 ml of water. A solution of 4-cyanopyridine (35 mmol, 3.64 g) in 34 ml of ethanol was then added, and the mixture stirred under reflux for 6 h. The precipitate formed was filtered off and recrystallized from ethanol; yield 71%, m.p. 209°C. ^{1}H NMR (DMSO-d_6, TMS, 250 MHz); δ ppm=10.3 (s, 1H, O–H); 8.67 (d, J=6.20 Hz, 2H, arom. H); 7.76 (d, J=6.20 Hz, 2H, arom. H); 3.70 (s, 2H, NH_2). ^{13}C NMR (DMSO-d_6, TMS, 62.9 MHz); δ ppm=149.7; 119.8 (arom. C); 149.1 (quaternary C of the amidoxime group); 140.6 (quaternary arom. C). IR

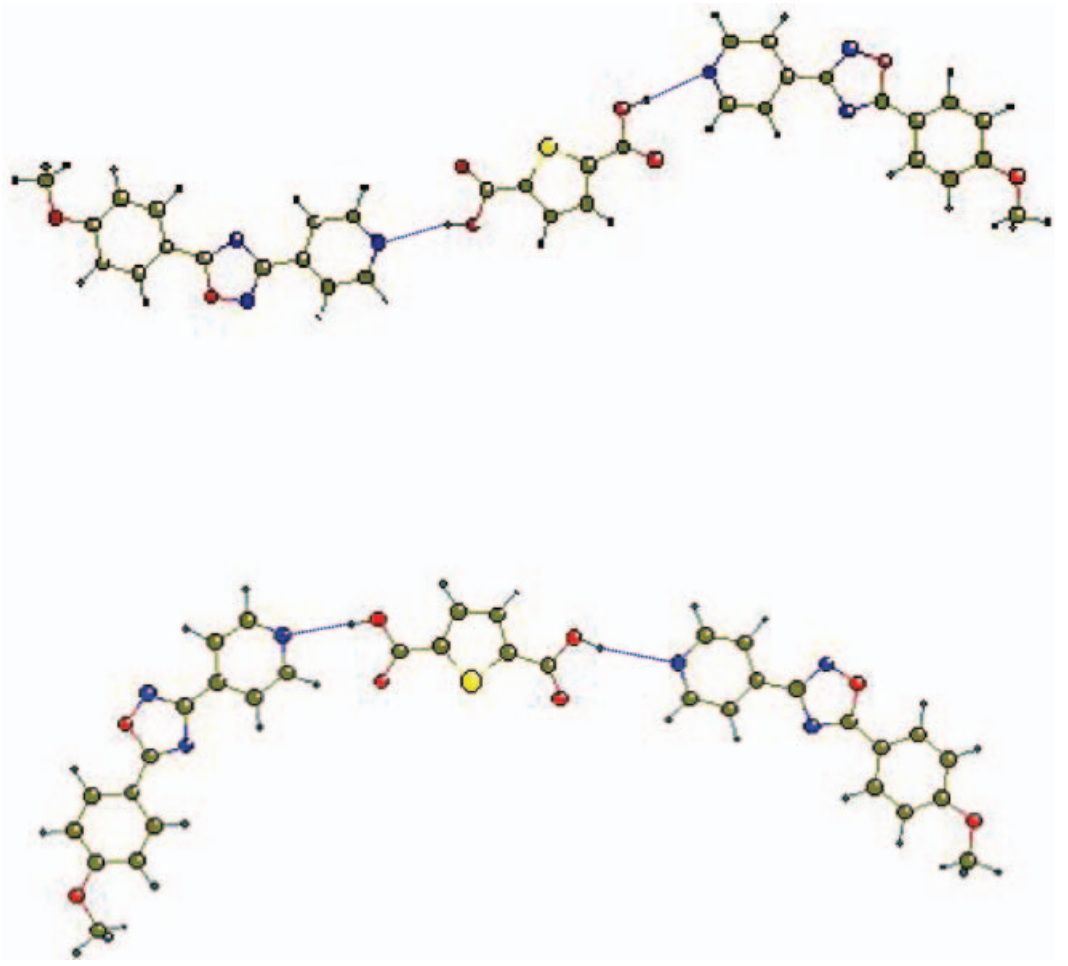


Figure 6. Diagram of the conformations of the hydrogen bonded complexes **3**: for details see text.

(KBr disk); cm^{-1}=3456, 3311 (N–H); 3150 (O–H); 1633 (C=N and C=C).

3.2.2. 3-(4-Pyridyl)-5-(4-n-alkoxy)phenyl-1,2,4-oxadiazoles (2a–e) [13]. As a general method, a solution of amidoxime **1** (7.3 mmol, 1.0 g) and methyl 4-*n*-alkoxybenzoate (14 mmol) in 20 ml of anhydrous ethanol was added to a stirred solution of sodium ethoxide (0.18 g, 7.8 mmol of sodium in 15 ml of anhydrous ethanol). The mixture was stirred and heated under reflux for 8 h. It was then cooled and the precipitate formed was filtered off and washed with ethanol. The solid was then suspended in 250 ml of water, stirred for 15 min, collected by filtration and recrystallized from ethanol. yields: **2a** 83%; **2b** 64%; **2c** 42%; **2d** 41%; **2e** 39%.

2a: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm=8.79 (d, J=4.54 Hz, 2H, pyridine ring); 8.13 (d, J=6.90 Hz, 2H, benzene ring); 8.01 (d, J=4.50 Hz, 2H, pyridine ring); 7.03 (d, J=6.94 Hz, 2H, benzene ring); 4.03 (t, J=6.56 Hz, 2H, $OC\underline{H}_2$); 1.76–1.37 (m, 8H, 4 CH_2); 0.93 (t, J=7.04 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm=176.3, 167.1, 163.0, 134.5, 116.0 (quaternary arom. C); 150.5, 130.0, 121.2, 115.0 (arom. C); 68.3 ($O\underline{C}H_2$); 31.4–13.2 (aliph. C). IR (KBr disk); cm^{-1}=3020 (C_{sp2}–H); 2949.8 (C_{sp3}–H); 1608.1 (C=C and C=N).

2b: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm=8.74 (d, J=5.97 Hz, 2H, pyridine ring); 8.05 (d, J=6.87 Hz, 2H, benzene ring); 7.95 (d, J=6.05 Hz, 2H, pyridine ring); 6.95 (d, J=6.91 Hz, 2H, benzene ring); 3.97 (t, J=6.56 Hz, 2H, $OC\underline{H}_2$); 1.76–1.31 (m, 10H, 5 CH_2); 0.88 (t, J=6.61 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm=176.2, 167.1, 163.0, 134.5, 115.9 (quaternary arom. C); 150.5, 123.0, 121.2, 114.9 (arom. C); 68.3 ($O\underline{C}H_2$); 31.6–13.9 (aliph. C). IR (KBr disk); cm^{-1}=3025 (C_{sp2}–H); 2921.3 (C_{sp3}–H); 1607.4 (C=C and C=N).

2c: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm=8.77 (d, J=5.54 Hz, 2H, pyridine ring); 8.09 (d, J=6.10 Hz, 2H, benzene ring); 7.98 (d, J=5.52 Hz, 2H, pyridine ring); 6.99 (d, J=6.15 Hz, 2H, benzene ring); 4.00 (t, J=7.38 Hz, 2H, $OC\underline{H}_2$); 1.82–1.28 (m, 12 H, 6 CH_2); 0.87 (t, J=6.88 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm=176.4, 167.2, 163.0, 134.6, 116.0 (quaternary arom. C); 150.6, 130.1, 121.3, 115.0 (arom. C); 68.4 ($O\underline{C}H_2$); 31.7–14.0 (aliph. C). IR (KBr disk); cm^{-1}=3030 (C_{sp2}–H); 2923.3 (C_{sp3}–H); 1608.5 (C=C and C=N).

2d: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm=8.85 (d, J=5.70 Hz, 2H, pyridine ring); 8.15 (d, J=4.90 Hz, 2H, benzene ring); 8.08 (d, J=5.72 Hz, 2H, pyridine ring); 7.06 (d, J=4.91 Hz, 2H, benzene ring); 4.06 (t, J=6.75 Hz, 2H, $OC\underline{H}_2$); 1.81–1.31 (m, 14H, 7 CH_2); 0.92 (t, J=7.00 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm=176.4, 167.1, 163.1, 135.0, 115.9 (quaternary arom. C); 150.2, 130.1, 121.5, 115.0 (arom. C); 68.4 ($O\underline{C}H_2$); 31.8–14.0 (aliph. C). IR (KBr disk); cm^{-1}=3025 (C_{sp2}–H); 2921.2 (C_{sp3}–H); 1610.4 (C=C and C=N).

2e: ^{1}H NMR ($CDCl_3$, TMS, 250 MHz); δ ppm=8.86 (d, J=4.80 Hz, 2H, pyridine ring); 8.18 (d, J=11.4 Hz, 2H, benzene ring); 8.08 (d, J=4.79 Hz, 2H, pyridine ring); 7.10 (d, J=11.42 Hz, 2H, benzene ring); 4.10 (t, J=6.54 Hz, 2H, $OC\underline{H}_2$); 1.88–1.34 (m, 16H, 8 CH_2); 0.94 (t, J=6.34 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$, TMS, 62.9 MHz); δ ppm=176.4, 167.1, 162.9, 135.0, 116.4 (quaternary arom. C); 150.5, 130.1, 121.4, 115.0 (arom. C); 68.4 ($O\underline{C}H_2$); 31.8–14.1 (aliph. C). IR (KBr disk); cm^{-1}=3020 (C_{sp2}–H); 2924.2 (C_{sp3}–H); 1608.1 (C=C and C=N).

3.2.3. Preparation of the hydrogen-bonded complexes (3a–e). The hydrogen-bonded complexes were prepared by slow evaporation of a tetrahydrofuran solution containing 2,5-thiophene dicarboxylic acid, as proton donor, and compounds of the series **2a**–**e**, as proton acceptor moieties in 1:2 molar ratio, followed by drying *in vacuo* at 60°C. Before evaporation the solutions were stirred at room temperature for 24 h.

Acknowledgement

This work was supported by FONDECYT (Grant 1000521) and 'Dirección de Investigación, Universidad de Concepción'.

References

[1] C.M. Paleos, D. Tsiourvas. *Angew. Chem. Int. ed. Engl.*, **34**, 1696 (1995).
[2] C.M. Paleos, D. Tsiourvas. *Liq. Cryst.*, **28**, 1127 (2001).
[3] H. Prade, R. Miethchen, V. Vill. *J. prakt. Chem.*, **337**, 427 (1995).
[4] Y. Tian, X. Xu, Y. Zhao, X. Tang, T. Li. *Liq. Cryst.*, **22**, 87 (1997).
[5] Z. Sideratou, D. Tsiourvas, C.M. Paleos, A. Skoulios. *Liq. Cryst.*, **22**, 51 (1997).
[6] M. Fukumasa, K. Takeuchi, T. Kato. *Liq. Cryst.*, **24**, 325 (1998).
[7] H.-C. Lin, J.-M. Shiaw, C.-Y. Wu, C. Tsai. *Liq. Cryst.*, **27**, 1103 (2000).
[8] B. Gündogan, K. Binnemans. *Liq. Cryst.*, **27**, 851 (2000).
[9] S. Pisupati, P.A. Kumar, V.G.K.M. Pisipati. *Liq. Cryst.*, **27**, 665 (2000).
[10] M. Parra, J. Alderete, C. Zúñiga, V. Jiménez, P. Hidalgo. *Liq. Cryst.*, **30**, 297 (2003).
[11] X. Song, J. Li, Sh. Zhang. *Liq. Cryst.*, **30**, 331 (2003).
[12] V.S. Bezborodov, P.F. Petrov, V.I. Lapanik. *Liq. Cryst.*, **20**, 785 (1996).
[13] L.F. Tietze, Th. Eicher. *Reactions and Syntheses in Organic Chemistry Laboratory,* translated by D. Ringe, pp. 312–313 (1989).
[14] S. Torgova, L. Karamysheva, A. Strigazzi. *Braz. J. Phys.*, **32**, 2B, 593 (2002).
[15] H.-C. Lin, J.-M. Shiaw, R.-Ch. Liu, Ch. Tsai, H.-H. Tso. *Liq. Cryst.*, **25**, 277 (1998).
[16] T. Kato, T. Uryu, F. Kaneuchi, Ch. Jin, J.M.J. Frechet. *Liq. Cryst.*, **4**, 1311 (1993).
[17] S. Bratoz, D. Hadzi, N. Sheppard. *Spectrochim Acta*, **8**, 249 (1956).
[18] V.P. Privalko, G.A. Puchkovskaya, E.N. Shermatov, A.A. Yakubov. *Mol. Cryst. liq. Cryst.*, **126**, 289 (1985).
[19] J.Y. Lee, P.C. Painter, M.M. Coleman. *Macromolecules*, **21**, 346 (1988).
[20] S.L. Johnson, K.A. Rumon. *J. phys. Chem.*, **69**, 74 (1965).
[21] S.E. Odikonov, A.V. Iogansen. *Spectrochim. Acta*, **32**, 1355 (1985).
[22] T. Kato, J.M.J. Frechet, P.G. Wilson, T. Saito, T. Uryu, A. Fujishima, C. Jin, F. Kaneuchi. *Chem. Mater.*, **5**, 1094 (1993).
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gil, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Peterson, J.A. Montogomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewaki, J.V. Ortiz, J.B. Foresman, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople. *Gaussian 94,* Revision B 2, Gaussian, Inc., Pittsburgh PA (1995).
[24] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart. *J. Am. chem. Soc.*, **107**, 3902 (1985).