STUDY THE PROPERTIES OF THERMOTROPIC LIQUID CRYSTALS INDUCED BY HYDROGEN BONDING BETWEEN PYRIDYL- HETEROCYCLIC DERIVATIVES AND BENZOIC ACID, 4-HEPTYLOXYBENZOIC ACID OR 4-OCTYLOXYBENZOIC ACID

Nasreen Raheem Jber
Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-Iraq.

Abstract

Synthesis of new derivatives of heterocyclic compounds such as (Triazoles, tetrazole, oxazole and thiadiazole). Liquid crystalline complexes have been obtained from binary mixtures of (4-pyridyl) heterocyclic derivatives with benzoic acid, 4-heptyloxychlorobenzoic acid or 4-octyloxybenzoic acid. The (4-pyridyl) heterocyclic derivatives are not mesomorphic, but the H-bonded complexes are showed droplets nematic texture which is developed from threaded nematic on slow heating. Their liquid crystalline properties were investigated by polarizing optical microscopy.

Keywords: Heterocyclic ring, Nematic liquid crystal.

Introduction

The first compounds found to exhibit liquid crystalline behaviour due to hydrogen bond formation were aromatic carboxylic acids[1-3]. These compounds dimerize through intermolecular hydrogen bonds leading to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity. However, the role of hydrogen bonding interactions in the formation and/or stabilization of liquid crystalline phases has been recognized only in the last ten years, and a large number of supramolecular liquid crystals obtained through hydrogen bonding interaction of complementary molecules have been extensively studied[4-6]. Mixtures of unlike hydrogen-bonded molecules producing liquid crystals frequently involve donor molecules derived from carboxylic acids and acceptor molecules derived from pyridine. These compounds were used as proton acceptors in the formation of mesomorphic H-bonded complexes with 4-n-alkyloxybenzoic acid as proton donor. We report here a new series of liquid crystalline complexes involving intermolecular hydrogen bonding between the 2-(4-pyridyl)-4-bromophenyl oxazole, 2-(4-pyridyl)- oxazol- 4-one, 2- (4-pyridyl) -4-bromophenyl thiazole, 2-(4-pyridyl)-thiazol-4-one, 5-(4-pyridyl)-1,2,3,4- tetrazole, 2-amino-5-(4-pyridyl)-thiadiazole and 2-mercapto-5-(4-prydiyl)-triazole with benzoic acid, 4-heptyloxybenzoic acid or 4-octyloxybenzoic acid. These hydrogen-bonded complexes contain only a single hydrogen bond in each system and showed an enantiotropic nematic phase.

Experimental

General

Melting points were determined on Gallenkamp melting point apparatus and were uncorrected. The IR spectra of the compounds were recorded on a shimadzu FTIR-8300 spectrometer as KBr disc. The ^{1}H NMR spectra were recorded on a *Brüker ACF 300* Spectrometer operating at 300 MHz in DMSO-d_6. The chemical shifts are reported in part per million (ppm) dowmfield internal tetramethylsilane (TMS) (chemical shift in δ values). The transition temperatures for all compounds were determined by optical microscopy using Olympus BX40 Microscope equipped with a Link–AmTH600 hot stage and PR600 controlle. ^{1}HNMR, elemental analysis, and microscopic observation were performed at the university of Exeter, England.

Synthesis of 4-alkoxybenzoic acid

Prepared from 4-hydroxy benzoic acid and appropriate alkyl halide according to Nygaard et al[7].

Synthesis of 3-(2-(4-pyridyl)-4-bromophenyl) oxazole (2)

A mixture of equimolecular amount of 4-bromophencyl bromide (0.47 g, 0.02 mole) and (2.44 g, 0.02 mole) of nicotine amide in alcoholic solution (20 mL ethanol) was refluxed for (8) hrs. and the reaction mixture was left to stirring overnight at room temperature. The end of the reaction was checked by T.L.C which showed the disappearance of amide spot and appearance of higher spot. Later excess ethanol was evaporated and the mixture was poured on crushed ice. The formed solid was filtered and recrystallized from a mixture of ethanol, water (1:1), a yellow precipitate was obtained with m.p. (169-171)° C, yield (62%).

2-(4-pyridyl)-oxazol-4-one (3)

A mixture of equimolecular amount of chloroacetic acid (0.94 g, 0.01 mole) and (1.22 g, 0.01 mole) of nicotine amide was dissolved in (25) mL absolute ethanol. The mixture was refluxed for (24) hrs. and the reaction mixture was left to stirring overnight at room temperature. The end of the reaction was checked by T.L.C which showed the disappearance of amide spot and appearance of higher spot. Later excess ethanol was evaporated and the mixture was poured on crushed ice. The formed solid was filtered and recrystallized from a mixture of ethanol, water (1:1). a pale yellow precipitate was obtained with m.p. (145-150)° C, yield (56%).

2-(4-pyridyl)-4-bromophenyl thiazole (5)

A mixture of equimolecular amount of 4-bromophencyl bromide (0.47 g, 0.02 mole) and (2.76 g, 0.02 mole) of 4-pyidine thioamide in absolute ethanol (20 mL) was refluxed for (8) hrs. and the reaction mixture was left to stirring overnight at room temperature. The end of the reaction was checked by T.L.C which showed the disappearance of thioamide spot and appearance of higher spot. A brown precipitate was obtained with m.p. (162-163) ° C, yield (43%).

2-(4-pyridyl)-thiazol-4-one (6)

A mixture of equimolecular amount of chloroacetic acid (0.94 g, 0.01 mole) and (1.38 g, 0.01 mole) of 4-pyidine thioamide was dissolved in (25) mL absolute ethanol. The mixture was refluxed for (24) hrs. and the reaction mixture was left to stirring overnight at room temperature. Later excess ethanol was evaporated and the mixture was poured on crushed ice. The formed solid was filtered and recrystallized from a mixture of ethanol, water (1:1). The end of the reaction was checked by T.L.C which showed the disappearance of thioamide spot and appearance of higher spot. The formed solid was filtered and recrystallized from a mixture of ethanol. A yellow precipitate was obtained with m.p. (132-134)° C, yield (48%).

5-(4-pyridyl)-1,2,3,4-tetrazole (8)

Refluxing 4-cyano pyridine (1.04 g, 0.01 mole) with sodium azide (1.33 g, 0.02 mole) and ammonium chloride in hot DMF (15 mL) for overnight with stirring, produced a dark brown precipitate with m.p. (180-183) ° C, yield (65%).

Nicotinyl thiosemicarbazone (11)

To a solution of nicotinyl chloride (0.02 mole) thiosemicarbazide (0.1 g. 0.001 mole) in absolute ethanol (20 mL) was added with continuous stirring. The resulting mixture was stirred overnight. The solid of white precipitate was filtered and recrystallize from ethanol to give white crystals of thiosemicarbazone derivative m.p. (230-232) °C, yield (85%).

2-mercapto-5-(4-prydiyl)-triazole (12)

Thiosemicarbazone compound (0.98 g, 0.005 mole) was refluxed with (2N) NaOH (2 mL) for 3 hrs. then coloed and filtered, the filtrate was acidified with glycial acetic acid to gave a solid which was recrystallized from ethanol, m.p. 222-225 ° C, yield (65%).

2-amino-5-(4-pyridyl)-thiadiazole (13)

Concentrated sulphuric acid (5 ml) was cooled to 0°C and stirred while thiosemicarbazone compound (0.39 g, 0.002 mole) was added portionwise. The mixture was stirred for 3 h in the cold and then allowed to warm to room temperature over a 1 h period. The solution was poured onto crushed ice and adjusted to pH 12 with concentrated sodium hydroxide. The

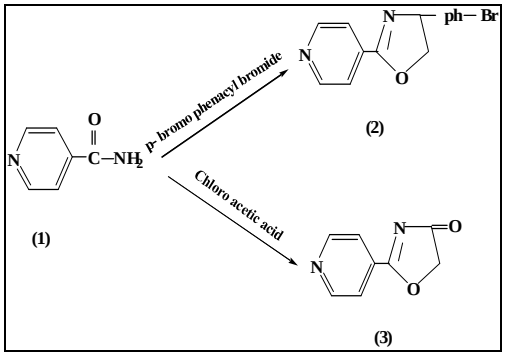
precipitated product was collected and recrystallized from ethanol yielding white solid (74%), m.p. (215-217)° C.

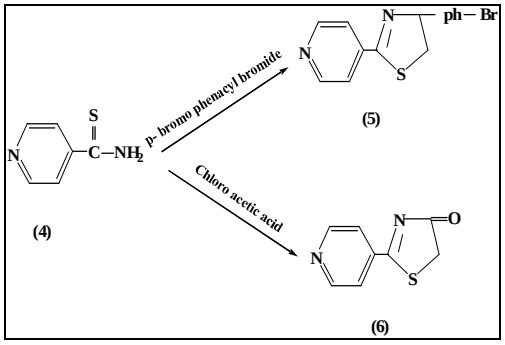
Preparation of the hydrogen-bonded complexes (14-20)$_{a,b}$

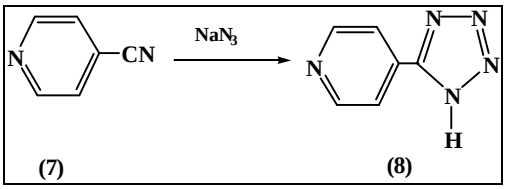
The hydrogen-bonded complexes were prepared by slow evaporation of a chloroform solution containing 4-alkoxybenzoic acid, as proton donor, and compounds (2,3,5,6,8,12 and 13) as proton acceptor moieties in 1:1 molar ratio, followed by drying in vacuo at 60°C. Before evaporation the solutions were stirred at room temperature for 24 h.

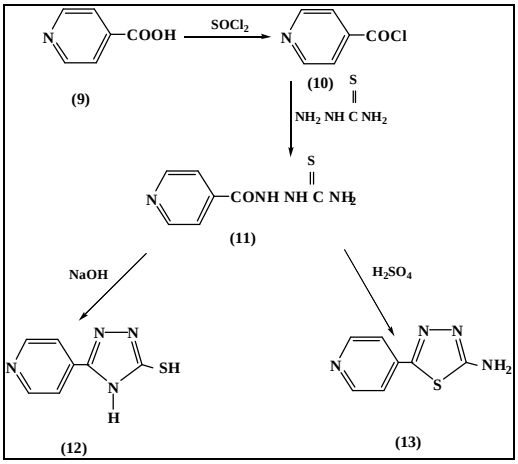
Results and Discussion

The 3- (2- (4-pyridyl)- 4-bromophenyl oxazole, 2-(4-pyridyl)- oxazol-4-one, 2- (4-pyridyl)- 4-bromophenyl thiazole, 2- (4-pyridyl)- thiazol-4-one, 5- (4-pyridyl)-1,2,3,4-tetrazole, 2-amino- 5- (4-pyridyl)- thiadiazole and 2-mercapto-5- (4-prydiyl)- triazole were synthesized and characterized. The proton donors benzoic acid, 4-heptyloxybenzoic acid and 4-octyloxybenzoic acid were prepared according to literature[7]. Fig.(1) shows the structures of the proton acceptors (2,3,5,6,8,12 and 13) and Fig.(2) shows their H-bonded complexes (14-20)$_{a,b}$ with the corresponding proton donor. The spectra of free *p-n*-alkoxybenzoic acids show two sharp bands at 1685 and 1695 cm^{-1} due to the ν (C=O) mode and a strong intense band at 3032 cm^{-1} assigned to the ν (OH) mode of the carboxylic acid group. This doubling nature of the carbonyl stretching mode may be attributed to the existence of dimeric benzoic acid at room temperature[8]. However, the corresponding spectra recorded in solution (chloroform) show an intense band at 1712 cm^{-1}, suggesting stabilization of the monomeric form of benzoic acid in solution[9]. To avoid further complications due to inter/intramolecular hydrogen bonding, the spectra of the complexes were compared with the free benzoic acids recorded in solution state. The infrared frequencies of (14-20)$_{a,b}$ complexes show a sharp band at ~ 1680 cm^{-1} due to the ν (C=O) mode of the benzoic acid moiety, which suggests its monomeric nature upon complexation. When compared to the free carboxylic acids spectra, the complexes show bathochromic shifts (~ 25 cm^{-1}) in the ν (C=O) mode of the benzoic acid moiety. These shifts strongly suggest the formation of intermolecular H-bonding between the–COOH group and the *nitrogen* of pyridine ring. Moreover, the band associated with the ν (OH) mode of the carboxylic acid group suffered a bathochromic shift upon complexation, which strongly supports the existence of H-bonding[10].









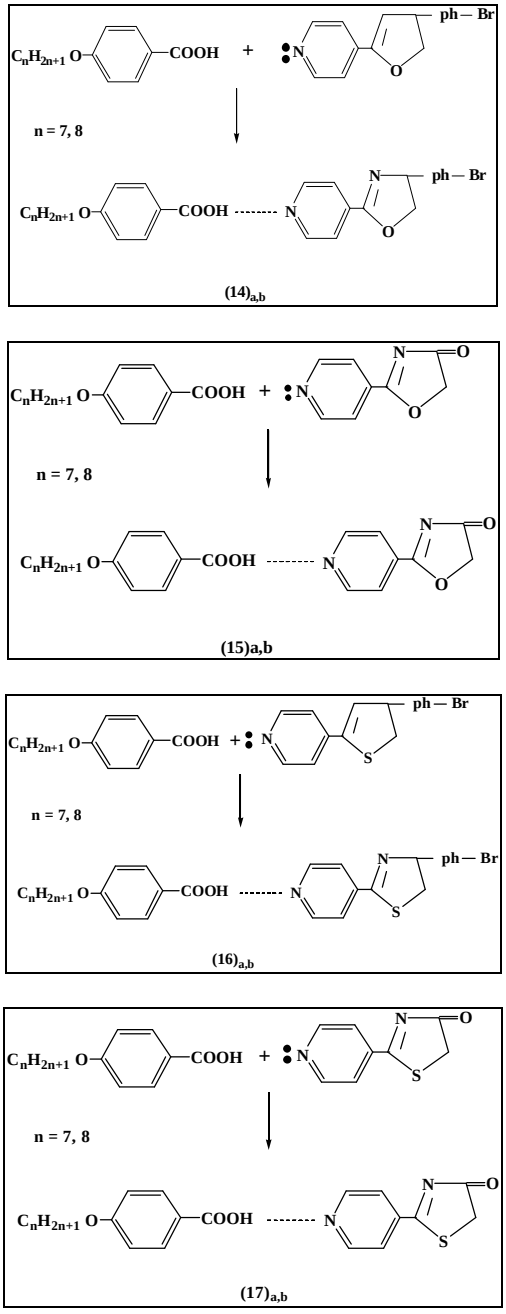


Fig.(1): The synthesize compounds.

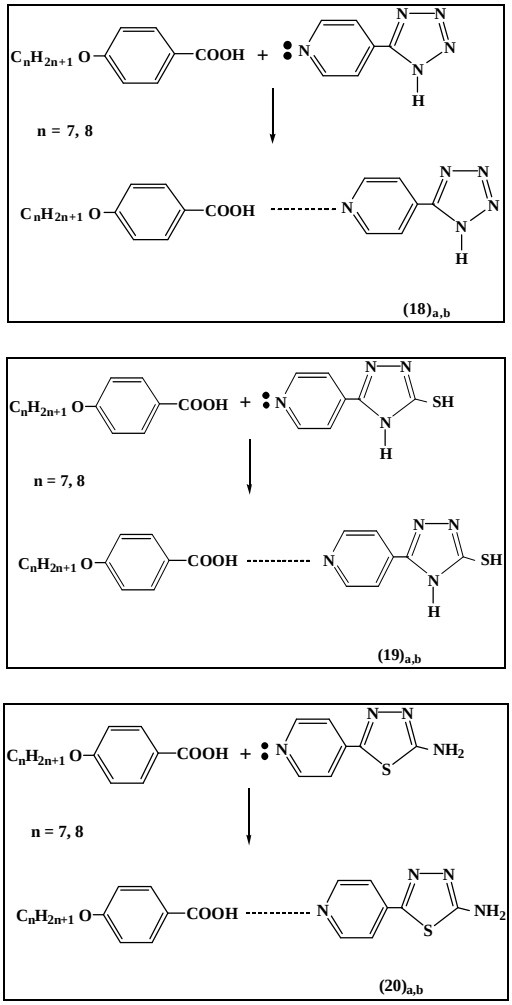


Fig. (2): Formation of H- bonded complexes.
Where a; n=7 and b; n=8.

3-(2-(4-pyridyl)-4-bromophenyl oxazole (2):

This compound was obtained by the reaction of nicotine amide with 4-bromophenacyl bromide as show in Fig.(1). The FTIR spectrum of the oxazole shows the following bands: 3065.7 cm^{-1} due to (C-H) aromatic band and bands at 1598.5, 1632.8 and 825 cm^{-1} due to (C=C), (C=N) and out of plane of para substituted vibrations, respectively. Also band at 1061.3 cm^{-1} due to (=C-O-C=). The proton ^{1}HNMR (DMSO-d_6, TMS, 300MHz): δ= 7.3 (2H, d, Ar-H); 6.9 (2H, d, Ar-H); 8.2 (d, 2H, d, Py); 7.8 (2H, d, Py); 3.4 (2H, d, cyclic CH_2); 3.6 (1H, s, cyclic CH) as show in Fig.(3).

2-(4-pyridyl)-oxazol-4-one (3):

This compound was obtained from treatment of nicotine amide with chloroacetic acid as show in Fig.(1). The FTIR spectrum of the 4-oxazolone shows band at 3361.3 cm^{-1} due to (OH) stretching for the enol form, (C-H) aromatic appeared at 3075.9 cm^{-1} bands at 1596.8 and 1613.6 cm^{-1} due to (C=C) and (C=N) vibrations, respectively.

2-(4-pyridyl)-4-bromophenyl thiazole (5):

This compound was obtained by the reaction of thionicotine amide with 4-bromophenacyl bromide as show in Fig. (1). The FTIR spectrum of the thiazole shows the following: band at 3040.1 due to (C-H) aromatic band and bands at 1584.9, 1635 and 834 cm^{-1} due to (C=C), (C=N) and out of plane of para substituted vibrations, respectively.

2-(4-pyridyl)-thiazol-4-one (6):

This compound was obtained from treatment of thionicotine amide with chloroacetic acid as show in Fig.(1). The FTIR spectrum of the 4-thiazolone shows the following bands: (C-H) aromatic appeared at 3080.4 cm^{-1}, the figure also shows bands at 1602.3 and 1635.4 cm^{-1} due to (C=C) and (C=N) vibrations, respectively. The proton ^{1}HNMR (DMSO-d_6, TMS, 300MHz): δ= 8.0 (d, 2H, d, Py); 7.6 (2H, d, Py); 3.6 (2H, d, cyclic CH_2) as show in Fig.(3).

5-(4-pyridyl)-1,2,3,4-tetrazole (8):

This compound was prepared by treating of 4-cyano pyridine with sodium azide and ammonium chloride in hot DMF. The FTIR spectrum of the prepared tetrazole from 4-cyano pyridine showed the disappearance of characteristic band of (**C≡N**) at 2243 cm^{-1}, and the appearance of new band of (C=N) at 1616.7 cm^{-1}. The spectrum also shows absorption at 3342.6 cm^{-1} for (N-H) stretching and dand at 1244.4 cm^{-1} for (N-N) stretching vibration. The proton ^{1}HNMR (DMSO-d_6, TMS, 300MHz): δ= 4.5 (1H, s, NH); 7.8 (d, 2H, d, Py); 7.3 (2H, d, Py) as show in Fig.(3).

2-mercapto-5-(4-prydiyl)-triazole (12):

This compound was obtained by the reaction of the prepared thiosemicarbazone derivative with NaOH under refluxing condition affected intramolecular cyclization through the loss of H_2O giving the thio-triazole derivative (12),as show in Fig.(1). The FTIR spectrum of the thio- triazole showed stretching band at 3300 cm^{-1} for (N-H) and 1656.7 cm^{-1} due to cyclic (C=N) also band at 1309.3 cm^{-1} for (C=S) and 2607.5 cm^{-1} corresponding to (S-H) group. The proton ^{1}HNMR (DMSO-d_6, TMS, 300MHz): δ= 4.6(1H, s, NH); 7.3 (1H, s, SH); 7.9 (d, 2H, d, Py); 7.4 (2H, d, Py) as show in Fig.(3).

2-amino-5-(4-pyridyl)-thiadiazole (13):

This compound was obtained by the reaction of the prepared thiosemicarbazone derivative with sulfuric acid at 120°C, Fig.(1), it was affected by intermolecular cyclization through the loss of H_2O, and giving the expected compound (13). The FTIR spectrum of the amino thiadiazole derivative showed stretching band at 3314; 3272 cm^{-1} for (NH_2); 3046 (C_{sp2}–H); and 1656.7 cm^{-1} due to cyclic (C=N). The proton ^{1}HNMR (DMSO-d_6, TMS, 300MHz): δ= 5.4 (2H, broad singlet, NH_2); 7.4 (d, 2H, d, Py); 6.8 (2H, d, Py) as show in Fig.(3).

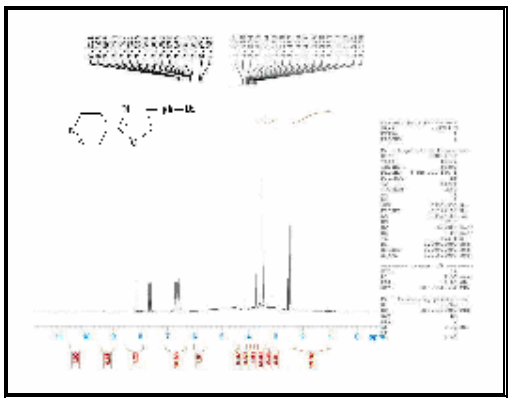
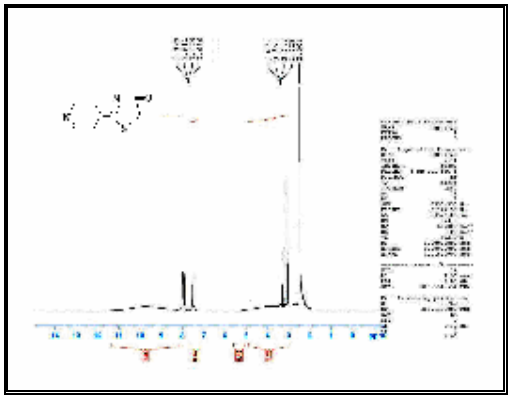
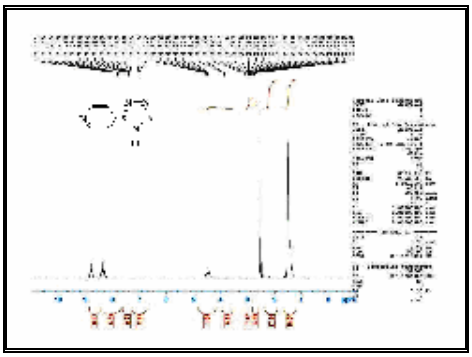
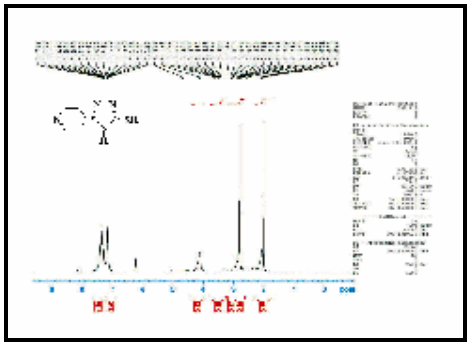
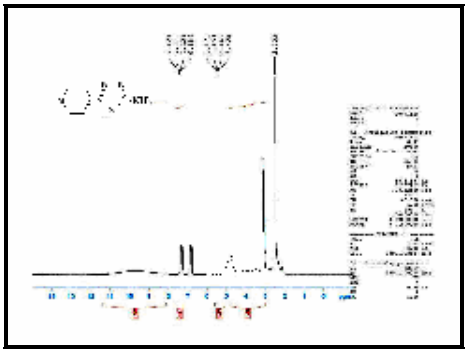


Fig.(3): ^{1}HNMR spectrum of compounds (2), (6), (8), (12) and (13).









Mesomorphic properties

The phases and their transition temperatures (Table (1)) were determined by textural observations[11] under a polarizing microscope equipped with a temperature control system at a scan rate of 0.1°C/minute. The *p*-*n*-alkoxybenzoic acids exhibit the nematic (marble) phase of the lower homologues (*n* = 3 to 6) and the smectic C (schilieren) phase of the higher members of the series.

All the H-bonded complexes of compounds $(14\text{-}20)_{a,b}$ show mesomorphic properties; the complexes behave as a single component and show clear phase transitions and homogeneous mesophases. Polarizing optical microscopy (POM) showed that all the compounds show droplets nematic texture which is developed from threaded nematic on slow heating, Fig.(4).

The heterocyclic derivatives (2,3,5,6,8,12 and 13) have a pyridine unit at the end of the rigid core are non-mesomorphic. The H-bonded complexes $(14\text{-}20)_{a,b}$ obtained by interaction of the compounds (2,3,5,6,8,12 and 13) with benzoic acid display liquid crystalline properties. The intermolecular H-bonding leads to a lengthening of the rigid-rod moiety, which in turn induces liquid crystallinity. The H-bonded complexes also have only one lateral alkoxy chain.

(Table 1) summarizes the mesomorphic behavior of the compounds $(14\text{-}20)_{a,b}$ with various heterocyclic ring.

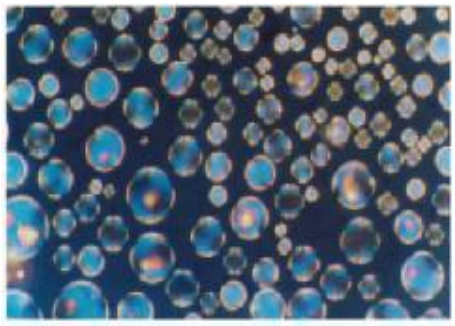
The mesophase stability of a liquid crystalline compound is dependent mainly on the intermolecular interactions, in which molecular polarity, polarizability and electronic factors play an important role[12] The H-bonded complexes $(14\text{-}20)_{a,b}$ display an enantiotropic nematic phase. (see Table 1 and Fig. 4).

Table (1)

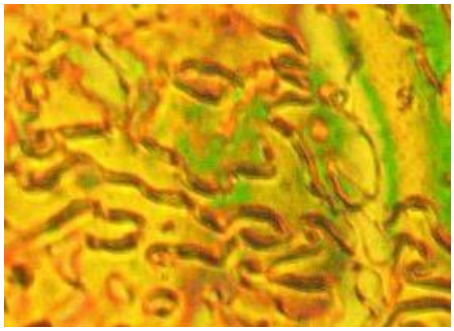
Melting points and Transition temperatures obtained from hot-stage polarizing microscopy of the compounds $(14\text{-}20)_{a,b}$

Comp. No.	*Transition*	*T°C*	*T °C Hot stage*
$(14)_a$	C → N N → I	148-150	147 152
$(14)_b$	C → N N → I	141-144	141 148
$(15)_a$	C → N N → I	132-134	130 135
$(15)_b$	C → N N → I	128-130	128 134
$(16)_a$	C → N N → I	145-147	144 148
$(16)_b$	C → N N → I	133-136	134 38
$(17)_a$	C → N N → I	118-120	117 122
$(17)_b$	C → N N → I	99-102	97 104
$(18)_a$	C → N N → I	168-172	167 173
$(18)_b$	C → N N → I	164-167	163 168
$(19)_a$	C → N N → I	201-205	200 206
$(19)_b$	C → N N → I	198-200	197 202
$(20)_a$	C → N N → I	200-204	198 206
$(20)_b$	C → N N → I	197-202	196 205

Where: C= crystal, N= nematic and I= isotropic.

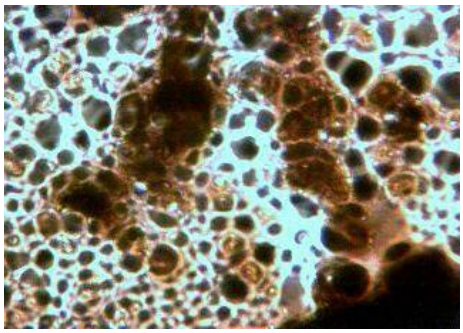


$(14)_a$

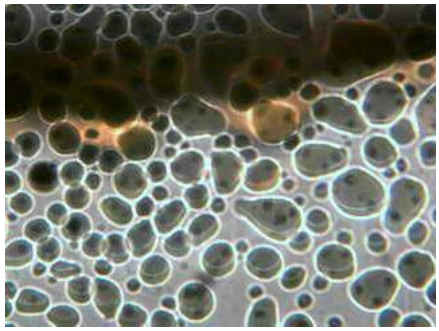


$(15)_b$

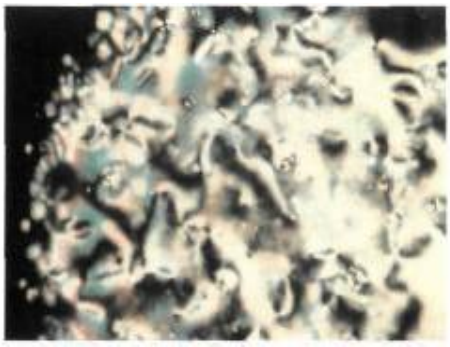
$(16)_b$



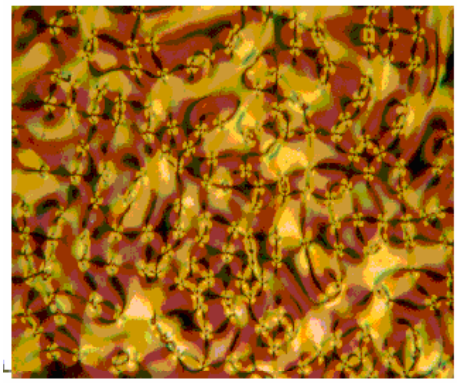
$(17)_a$



$(18)_a$



$(19)_b$



$(20)_b$

Fig. (4): Mesophase textures (nematic droplets)$(14)_a$, $(17)_a$, $(18)_a$, $(19)_b$ and $(20)_b$, and (threaded nematic texture) for $(15)_b$ and $(16)_b$ of H- bonded complexes.

Conclusion

Comparative thermal studies on the present series reveal that a nematic phase is induced in all the complexes. A possible explanation of the induction of this new phase may be molecular contributions originated from the intermolecular hydrogen bonding between the electron rich pyridine-nitrogen and –COOH groups.

References

[1] S. Singh, "Liquid Crystals: Fundamentals", World Scientific, London, 2008, pp. 96-97.

[2] H. Kelker, R. Hatz, "Handbook of Liquid Crystals", Verlag Chemie, Weinheim, 1980, pp. 59-63.

[3] M. Parra, P. Hidalgo, and J. Alderete, "New supramolecular liquid crystals induced by hydrogen bonding between pyridyl-1,2,4-oxadiazole derivatives and 2,5-thiophene dicarboxylic acid", Liquid Crystals, Vol. 32, No. 4, 2005, pp. 449-455.

[4] M. Parra, J. Alderete, C. Zu´n˜ iga, V. Jime´nez, P. Hidalgo., "Azo compounds and Schiff's bases derived from 5-(4-pyridyl)-2- amino- 1,3,4- thiadiazole: synthesis, mesomorphic properties and structural study by semi-empirical calculations", Liq. Cryst., Vol. 28, No. 11, 2001, pp. 1659-1666.

[5] M. He, R. J. Twieg, A. Fort, and L. Mager., "Synthesis and mesogenic properties of liquid crystals with a 1-biphenyl-4-methylene- 1,4- di, tetra or hexahydropyridine core unit", Liq. Cryst., Vol. 28, 2001, pp. 1127.

[6] M. Parra, P. Hidalgo, J. Barbera and J. Alderete, "Properties of thermotropic liquid crystals induced by hydrogen bonding between pyridyl- 1,2,4-oxadiazole derivatives and benzoic acid, 4-chlorobenzoic acid or 4-methylbenzoic acid", Liquid Crystals, Vol. 32, No. 5, 2005, pp. 573–577.

[7] G. Gray,"Molecular structure and the properties of liquid crystals", Academic press, New York, 1980, pp. 150-152.

[8] K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 4th edition, Interscience, New York, 1978, pp. 63-64.

[9] M. Parra, S. Hernandez, J. alderete and C. Zu´n˜ iga, "New Schiff's bases containing 1,3,4-thiadiazole and 1,3,4-oxadiazole units: a study of the effect of the heterocyclic ring and the position of the lateral alkoxy group on liquid crystalline properties", Liquid Crystals, Vol. 27, No. 8, 2000, pp.995-1000.

[10] Han, J. Wang, F. Zhang, L. Zhu, M. Pang and J. Meng, "Synthesis and mesomorphic behaviour of heterocycle-based liquid crystals containing 1,3,4-oxadiazole/ thiadia-zole and thiophene units", Liquid Crystals, Vol. 35, No. 10, 2008, pp. 1205 – 1214.

[11] M. Šepelj, A. Lesac, U. Baumeister, S. Diele, D. W. Bruce, and Z. Hameršak, "Dimeric Salicylaldimine-Based Mesogens with Flexible Spacers: Parity-Dependent Mesomorphism", American Chemical Society, Vol., 18, No. 8, 2006, pp. 2050-2058.

[12] G. Pelzl and W. Weissflog, "Mesophase Behaviour at the Borderline between Calamitic and 'Banana-shaped' Mesogens", Chemistry and Materials Science, Vol. 8, 2007, pp. 1-58.

الخلاصة

تم تحضير مشتقات جديدة من المركبات (ترايازول، تاترازول، اوكسازول و ثايادايازول). تم الحصول على معقدات ذات صفات بلورية سائلة من الخليط الثنائي لمشتقات الحلقات الغير متجانسة للـ 4-بريدايل مع الحوامض الكاربوكسيلية: 4-هبتايلوكسي حامض البنزويك او 4-اوكتايلوكسي حامض البنزويك. ان مشتقات الحلقات غير المتجانسة للـ 4-بريدايل لم تُظهر اي صفات بلورية سائلة بينما معقدات التآصر الهيدروجيني لهذه المركبات مع الحوامض الكاربوكسيلية اظهرات اطواراً نيماتية. تم التحقق من الصفات البلورية السائلة باستخدام المجهر البصري المستقطب.