Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Behavior of Some Novel Compounds Containing 1,3,4-Thiadiazole and 1,2,4-Triazole Rings

Jumbed H. Tomma [a], Ivan H. Rou'il [b] & Amar H. Al-Dujaili [a]

[a] Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq

[b] Department of Chemistry, College of Science, University of Al-Mustanseryia, Baghdad, Iraq

Version of record first published: 18 Mar 2009

To cite this article: Jumbed H. Tomma, Ivan H. Rou'il & Amar H. Al-Dujaili (2009): Synthesis and Mesomorphic Behavior of Some Novel Compounds Containing 1,3,4-Thiadiazole and 1,2,4-Triazole Rings, Molecular Crystals and Liquid Crystals, 501:1, 3-19

To link to this article: http://dx.doi.org/10.1080/15421400802697160

Mol. Cryst. Liq. Cryst., Vol. 501, pp. 3–19, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802697160

Synthesis and Mesomorphic Behavior of Some Novel Compounds Containing 1,3,4-Thiadiazole and 1,2,4-Triazole Rings

Jumbed H. Tomma[1], **Ivan H. Rou'il**[2], **and Amar H. Al-Dujaili**[1]
[1]Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq
[2]Department of Chemistry, College of Science, University of Al-Mustanseryia, Baghdad, Iraq

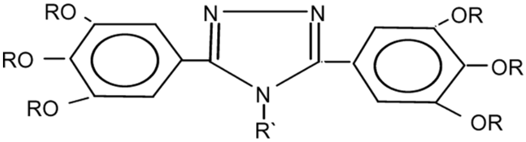
Two new mesogenic homologous series of liquid crystalline compounds containing 1,2,4-triazole and 1,3,4-thiadiazole in the molecule viz. 1,4-bis{3-[2-(4-alkoxy-benzelideneamino)-1,3,4-thiadiazole-5-ethylenethio]1,2,4-triazole-5-yl}phenyl and 5-(4-methoxyphenyl)-3-[2-(4-n-xybenzelidenamino)-1,3,4-thiadiazole-5-methylenethio]-1,2,4-triazole were synthesized by many step procedures. Both series have been characterized by elemental analysis, FT-IR, mass spectrometry, ^{1}H-NMR, and ^{13}C-NMR. Phase transition temperature and the thermal parameters were obtained from differential scanning calorimetery (DSC). The texture observations were performed under hot-stage polarizing optical microscopy (POM). All compounds of the first series exhibited an enantiotropic nematic mesophase. The first compound of the second series exhibited an enantiotropic nematic mesophase, and that with propyloxy terminal substituent shows one enantiotropic nematic phase on heating and a monotropic smectic A (SmA) phase on cooling, while the last two homologues exhibit a monotropic SmA phase. In contrast, the compound with an ethoxy terminal substituent does not show any liquid crystalline properties. The mesomorphic behavior has been analyzed in terms of structural property relationship.

Keywords: 1,3,4-thiadiazole; 1,2,4-triazole; mesomorphic; nematic phase; Schiff base; smectic phase

Address correspondence to Amar H. Al-Dujaili, Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq. E-mail: ahdujaili@yahoo.com

INTRODUCTION

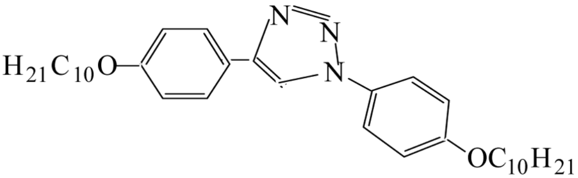
A relatively large number of liquid crystalline compounds containing heterocyclic units have been synthesized, and interest in such compounds is growing [1–5]. Several liquid crystalline compounds containing a heterocyclic ring have been reported [5–10]. Many series of these compounds containing 1,3,4-oxadiazole or 1,3,4-thiadiazole have been synthesized and studied [11–14]. The mesomorphic studies of triazole derivatives as potential materials are very limited, and little known examples of triazole based compounds exhibiting mesomorphic properties have been reported. A new type of five-member heterocyclic triazole (1) utilized as core group to generate room temperature disorder hexagonal columnar (Col_{hd}) mesophases is reported compared to other heterocyclic molecules like thiadiazole, oxadiazole and others [15].



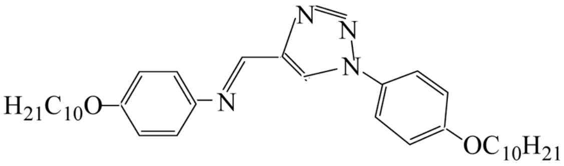
(1)

R′=benzyl; R=$(CH_2)_nH$, n = 6-8 and 10, 12; n = 14, (Col_{hd} 61.6°C I); n = 7, (Col_{hd} 66.5°C I); n = 8, (Col_{hd} 69.1°C I); n = 10, (Col_{hd} 62.7°C I); n = 12, (Col_{hd} 67.1°C I); n = 6, (Col_{hd} 74.8°C I).

Cristiano et al. [16] have reported the synthesis and mesomorphic properties of 1,4-diaryl and Schiff's base [1,2,3]-triazole derivatives (2). They found that all compounds exhibited the SmC phase.



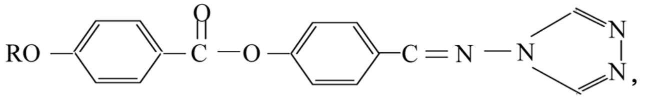
CrI 138.2°C CrII 144.2°C SmC 164.1°C SmA 167.2°C I



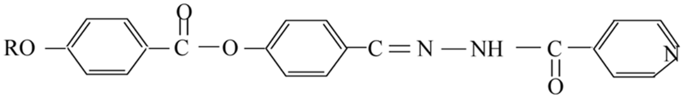
(2)

CrI 136.3°C CrII 184.9°C SmC 246.1 I

Mesogenic compounds containing 1,2,4-triazole and isonicotinic acid ring at the terminus of the molecule (3) have recently been reported [17].



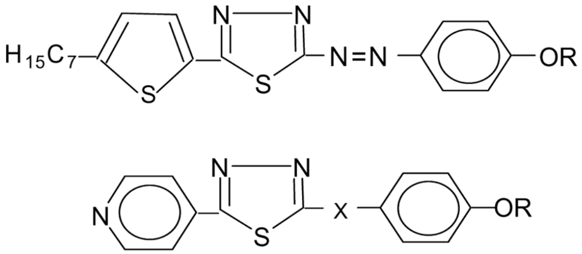
where $R=C_nH_{2n+1}$, n = 1-8, and 10, 12, 14, 16; n = 1, (Cr 226°C N 243°C I); n = 2, (Cr 213°C N 239°C I); n = 3, (Cr 209°C N 238°C I); n = 4, (Cr 204°C N 232°C I); n = 5, (Cr 196°C N 229°C I); n = 6, (Cr 189°C N 226°C I); n = 7, (Cr 177°C N 219°C I); n = 8, (Cr 162°C N 215°C I); n = 10, (Cr 164°C N 208°C I); n = 12, (Cr 76°C SmC 166°C N 207°C I); n = 14, (Cr 63°C SmA 142°C N 205°C I); n = 16, (Cr 30°C SmC 128°C N 191)



(3)

where $R=C_nH_{2n+1}$, n = 1-8, and 10, 12, 14, 16; n = 1, (Cr 201°C I); n = 2, (Cr 195°C I); n = 3, (Cr 192°C I); n = 4, (Cr 82°C N 190°C I); n = 5, (Cr 98°C N 184°C I); n = 6, (Cr 121°C N 177°C I); n = 7, (Cr 129°C N 176°C I); n = 8, (Cr 142°C N 169°C I); n = 10, (Cr 129°C SmC 159°C N 167°C I); n = 12, (Cr 113°C SmA 132°C N 161°C I); n = 14, (Cr 101°C SmC 144°C N 157°C I); n = 16, (Cr 87°C SmC 139°C N 152°C I).

A few mesomorphic homologous series containing two types of heterocyclic units in the same molecule (4) have been studied by Parra et al. [17,18].



(4)

where x=N=CH, $R=C_nH_{2n+1}$, n = 5-10; n = 5, (Cr 149.5°C I (136.1°C) SmA); n = 6, (Cr 149.3°C I (129.1°C) SmA); n = 7, (Cr 152.4°C I (129.1°C) SmA); n = 8 (Cr 147.5°C SmA 160.8°C I); n = 9 (Cr 141.9°C SmA 163.3°C I); n = 10 (Cr 142.1°C SmA 165.6°C I); where x=N=N, $R=C_nH_{2n+1}-$, n = 5-10; n = 5, (Cr 155.2°C I); n = 6, (Cr 155.3°C I);

n = 7, (Cr 157.4°C I); n = 8 (Cr 150.5°C I); n = 9 (Cr 144°C I (136°C) N); n = 10, (Cr 140°C I (136°C) N).

To our knowledge, there is no study for the preparation and mesomorphic properties of Schiff bases containing thiadiazole and triazole units in the same molecule. In light of this, it seems of interest to design new molecules having the above structure and providing further information concerning the relative importance of rigidity, linearity, polarizability, and enhancement of luminescent by the heterocyclic rings in mesophase stability.

EXPERIMENTAL

Reagents and Technique

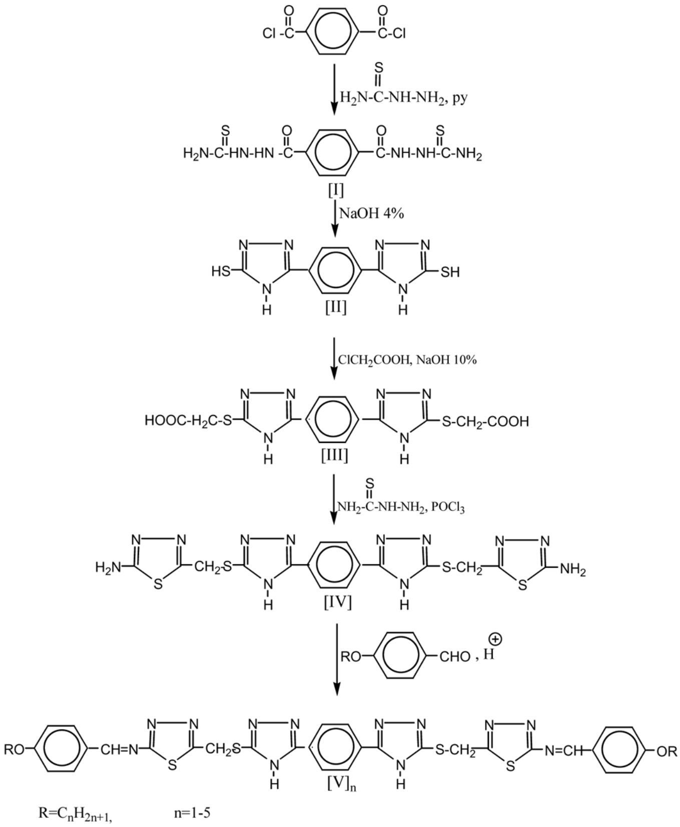
All chemicals and solvents were of reagent grade (Aldrich Chemicals Co.) and used without further purification. Elemental analysis (C, H, N) were carried out using a Perkin-Elmer model 2400 instrument. Infrared spectra were recorded with a Shimadzu 8000 FT-IR spectrophotometer in the wave number range 4000–400 cm^{-1} with samples embedded in KBr disc. ^{1}H-NMR spectra were obtained with a Varian Mercury plus spectrometer 400 MHz instrument using suitable deuterated solvent and TMS as internal standard. 13C-NMR spectra of the compound were recorded on a Varian Mercury plus 100 MHz spectrometer. Mass spectra were recorded on IEOL JMS-7 high resolution instrument. The optical behavior observations were made using Olympus BX40 microscope equipped with a Leitz Laborlux 12 Pols hot stage and PR600 controller. The textures shown by the compounds were observed using polarized light with crossed polarizers with the sample in a thin film sandwiched between a glass slide and cover slip. Differential scanning calorimetry (DSC) measurements were conducted with TA instruments Q1000 DSC, Ramp rate: 10 degree centigrade per minute under nitrogen atmosphere. Temperature and heat flow calibrated with standard indium of purity $< 99.99\%$.

Synthesis

The reaction sequences leading to the formation of compounds of the two series $[V]_n$ and $[X]_n$ are outlined in Schemes 1 and 2, respectively.

Synthesis of 1,4-Terphthalic Acid Thiosemicarbazide [I]

To a stirring solution of thiosemicarbazide (0.91 g, 0.01 mol) in dry pyridine 15 mL, at −5°C, a solution of terphthaloyl chloride (1.020 g, 5 mmol) in dry benzene 15 mL was added dropwise. The stirring was

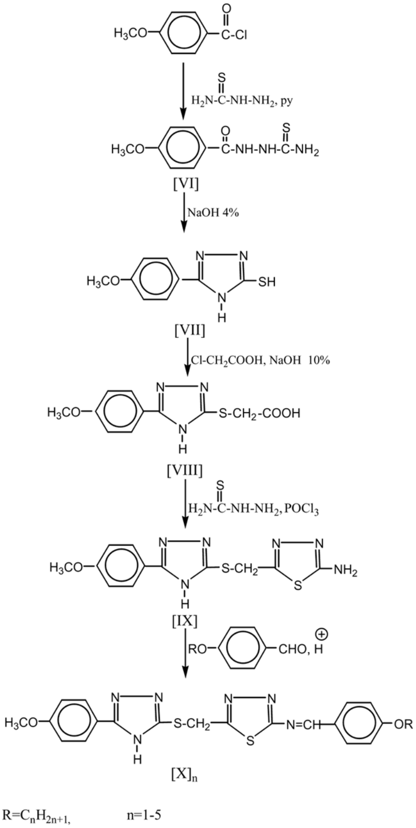


SCHEME 1 The preparation route of series $[V]_n$.

continued for half an hour at $-5°C$ and then overnight at room temperature. The solvent was evaporated. To the residue, water 30 mL was added, the precipitate was filtered and recrystallized from ethanol [20] to yield 70%, m.p. = 262–265°C. FT-IR (KBr, cm^{-1} 1182 ($\nu_{C=S}$); 1674 ($\nu_{C=O}$, amide); three bands at 3440, 3284, and 3182 ($\nu_{N\text{-}H}$ of amide and amine groups, respectively).

Synthesis of 1,4-Bis(3-mercapto-1,2,4-triazole-5-yl)phenyl [II]

A stirring solution of compound [I] (0.40 g, 0.01 mol) and 10 mL 4% aqueous sodium hydroxide solution was refluxed for 3–4 hours. After that, the mixture was filtered, and the filterate was acidified with dilute hydrochloric acid. The precipitate was filtered and washed several times with water [21], yield 85%. m.p. > 300°C. FT-IR (KBr,



SCHEME 2 The preparation route of series $[X]_n$.

cm^{-1}): 1224 ($\nu_{C=S}$); 1639 ($\nu_{C=N}$ of triazole moiety); 2630 ($\nu_{S\text{-}H}$); 3446 ($\nu_{N\text{-}H}$ of triazole moiety). ^{1}H NMR (DMSO), ppm: $\delta = 3.19$–3.59 broad (s, 2H, NH); 8.05–8.11 (s, 4H, arom. H); 13.66–14.12 (s, broad, 2H, SH). Ms: $m/z + 1 = 277$.

Synthesis of 1,4-Bis(3-thioaceticacid-1,2,4-triazole-5-yl)phenyl [III]

To a stirring of α-chloroacetic acid (1.64 g, 0.02 mol) in 10% aqueous sodium hydroxide 10 mL, a solution of compound [II] (0.01 mol) in 10% aqueous solution of sodium hydroxide, 10 mL was added, the mixture was refluxed for three hours. After cooling, the solution was acidified with concentrated hydrochloric acid. The precipitate was filtered and recrystallized from ethanol [22] to yield 75%, m.p. = 277°C. FT-IR, (KBr, cm^{-1}): 1693 ($\nu_{C=O}$, carboxylic moiety); 2927 ($\nu_{C\text{-}H}$ aliphatic); 2750–3400 ($\nu_{O\text{-}H}$ broad of carboxylic acid). ^{1}H NMR (DMSO), ppm: $\delta = 4.15$ (s, 4H, SCH_2); 4.99–5.19 (s broad, 2H, NH); 8.05–8.19 (s, 4H, arom. H); 10.69 (s, 2H, COOH). MS: $m/z + 1 = 393$.

Synthesis of 1,4-Bis[3-(2-amino-1,3,4-thiadiazole-5-methylenethio)1,2,4-triazole-5-yl]phenyl [IV]

A mixture of compound [III] (1.66 g, 0.01 mol), thiosemicarbazide (1.82 g, 0.02 mol), phosphorusoxychloride 10 mL was refluxed gently for (48) hours. After cooling, 50 mL of water was added in portions with stirring. The precipitate was filtered, washed with hot water, recrystallized from DMF-water [20], yield 65%, m.p. = 250°C. FT-IR (KBr, cm^{-1}): 1631 ($\nu_{C=N}$ of thiadiazole moiety); 1639 ($\nu_{C=N}$ of triazole moiety); two peaks at 3168, 3300 (ν_s and ν_{as} of NH_2 group). ^{1}H NMR (DMSO), ppm: $\delta = 4.02$–4.10 (broad s, 2H, NH); 4.65 (s, 4H, SCH_2); 7.25–7.56 (broad s, 4H, NH_2); 8.15–8.20 (s, 4H, arom. H). MS: $m/z + 1 = 503$.

Synthesis of 1,4-Bis{3-[2-(4-alkoxybenzelideneamino)-1,3,4-thiadiazole-5-methylenethio]1,2,4-triazole-5-yl}phenyl $[V]_n$

A mixture of [IV] (0.01 mmol), excess of 4-substitutedbenzaldehyde, and three drops of glacial acetic acid was heated in an oil bath at 150°C for 2 hours. The residue was cooled and crystallized from petroleum ether (40–60°C), giving yellow leaflets.

Data Compound $[V]_3$

Yield (60–80%). M.P. = 105°C. Calc. for $C_{36}H_{38}O_2N_{12}S_4$;, C, 54.41; H, 4.28; N, 21.16; Found: C, 54.33; H, 4.17; N, 21.06. MS: $m/z + 2 = 796$. FT-IR (KBr, cm^{-1}): 1665 ($\nu_{C=N}$, imine); 2875–2964 ($\nu_{C\text{-}H}$ aliphatic). ^{1}H NMR (DMSO): $\delta = 0.91$–1.02 ppm (t, 6H, CH_3); 1.62–1.79 (m, 4H, CH_2); 3.78–4.15 (t, 4H, Ph-OCH_2); 4.65 (s, 4H, SCH_2); 4.23 (weak s, 2H, N-H); 6.98–7.85 (d-d, 8H, Ar-H of phenyl ring attached OR); 8.18 (s, 4H, Ar-H of phenyl ring between triazole rings); 8.58 (s weak, 2H, imine group). ^{13}C NMR (DMSO), 14.72 ppm (CH_3), 23.11–35.61 ppm (CH_2), 30.31–32.41 ppm (C-S), 123.50–166.21 ppm (Ar-C), 159.11 ppm (C=N), 139.21–161.79 ppm (Triazole-C).

Synthesis of N-(4-Methoxybenzoyl)-thiosemicarbazide [VI]

This compound was prepared by using the same procedure given for compound [I] to yield 95%, m.p. = 226°C. FT-IR (KBr, cm^{-1}) 1184

($\nu_{C=S}$); 1664 ($\nu_{C=O}$, amide); three bands at 3402, 3253, and 3145 ($\nu_{N\text{-}H}$ of amide and amine groups, respectively).

Synthesis of 5-(4-Methoxyphenyl)-1,2,4-triazole-3-thiol [VII]

This compound was prepared by using the same procedure given for compound [II] to yield 80%, m.p. = 259–262°C. FT-IR (KBr, cm^{-1}): 1612 (νC=N of triazole moiety); 1224 ($\nu_{C=S}$); 2682 ($\nu_{S\text{-}H}$); 3242 ($\nu_{N\text{-}H}$ of triazole moiety). Ms: m/z = 207.

Synthesis of 5-(4-Methoxyphenyl)-3-thioaceticacid-1,2,4-triazole [VIII]

This compound was prepared by using the same procedure given for compound [III] to yield 82%, m.p. = 204–206°C. FT-IR (KBr, cm^{-1} : 1679 ($\nu_{C=O}$, carboxylic moiety); 2837–2939 ($\nu_{C\text{-}H}$ aliphatic); 2777–3205 ($\nu_{O\text{-}H}$ broad of carboxylic acid). ^{1}H NMR (DMSO), ppm: $\delta = 3.85$ (s, 3H, OCH_3); 4.09 (s, 2H, SCH_2); 5.05 (weak s, 1H, NH); 7.05-7.92 (d-d, 4H, arom. H); 10.29 (weak s, 1H, COOH). Ms: m/z = 265.

Synthesis of 5-(4-Methoxyphenyl)-3-(2-amino-1,3,4-thiadiazole-5-methylenethio)-1,2,4-triazole [IX]

This compound was prepared by using the same procedure given for compound [IV] to yield 63%, m.p. = 145°C. FTIR(KBr, cm^{-1}): 1614 ($\nu_{C=N}$ of thiadiazole moiety); 1630 ($\nu_{C=N}$ of triazole moiety); two peaks in the region 3100–3380 (ν_s and ν_{as} of NH_2 group). ^{1}H NMR (DMSO), ppm: $\delta = 3.88$ (s, 3H, OCH_3); 4.02 (s, 2H, SCH_2); 4.62 (s, 1H, NH); 6.15 (weaks, 2H, NH_2); 6.95–8.12 (d-d, 4H, arom. H). ^{13}C NMR (DMSO), 14.69 ppm (OCH3), 30.11–36.71 ppm (C-S), 40.38 ppm (C-N), 55.92 ppm (C-O), 115.10–129.41 ppm (Ar-C), 161.31 ppm (C=N).

Synthesis of 5-(4-Methoxyphenyl)-3-[2-(4-n-alkoxybenzelidenamino)-1,3,4-thiadiazole-5-methylenethio]-1,2,4-triazole $[X]_n$

The compounds of this series were prepared by using the same procedure given for compounds $[V]_n$.

Data Compound $[X]_1$

Yield 58–67%. M.P. 117°C. Calc. for $C_{20}H_{18}O_2N_6S_2$;, $_C$, 54.79; H, 4.11; N, 19.18; Found: C, 54.65; H, 4.01; N, 20.75. MS: m/z + 2 = 796. FTIR

(KBr, cm^{-1}): 1680 ($\nu_{C=N}$, imine); 2848–2920 ($\nu_{C\text{-}H}$ aliphatic). ^{1}H NMR (DMSO): $\delta = 3.57$ ppm (s, 1H, N-H); (two singlet near together at 3.71 and 3.76 ppm, 6H, OCH_3); 4.55 ppm (s, 2H, SCH_2); 6.91–7.19 ppm (d-d, 4H, Ar-H of phenyl ring attached triazole ring); 7.81–8.09 ppm (d-d, 4H, arom. H); 9.82 ppm (s, 1H, imine group). ^{13}C NMR (DMSO), 14.36 ppm (OCH_3), 32.41 ppm (C-S), 41.14 ppm (C-N), 124.51–166.93 ppm (Ar-C), 161.26 ppm (C=N), 142.11–163.11 ppm (Triazole-C).

RESULTS AND DISCUSSION

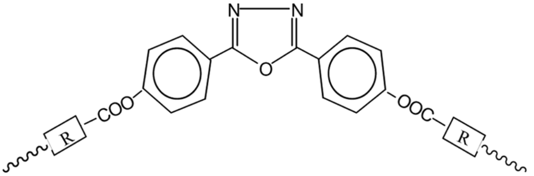
Schemes 1 and 2 outline the synthesis of the ten compounds of the two series $[V]_n$ and $[X]_n$. The elemental analyses of series $[V]_n$ and $[X]_n$ compounds synthesized above are shown in Table 1. The observed values are in agreement with theoretical values indicating structure of respective compounds. All compounds were also characterized by FT-IR, ^{1}H, ^{13}C NMR, and mass spectroscopy.

Mesomorphic Behavior

Many examples of nonlinear mesogens were prepared, starting with Vorlander and Apel [23] who considered nonlinear mesogens prepared. Dingemans and Samulski [24] used the term boomerang-shaped mesogen to characterize the more rigid and better defined nonlinearity with mesogens derived from 2,5-bis-p-hydroxyphenyl-1,3,4-oxadiazole having 134° bend in the mesogenic core (5).

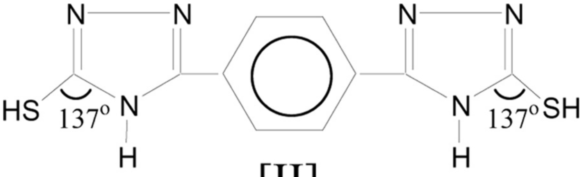
TABLE 1 Elemental Analysis Data for the Series $[V]_n$ and $[X]_n$

Compound	Molecular formula	Molecular weight (g/mole)	Analysis % found (calcd.)		
			C	H	N
$[V]_1$	$C_{32}H_{26}O_2N_{12}S_4$	738	51.79 (52.03)	3.47 (3.52)	22.71 (22.76)
$[V]_2$	$C_{34}H_{30}O_2N_{12}S_4$	766	53.19 (53.26)	3.85 (3.92)	21.80 (21.93)
$[V]_3$	$C_{36}H_{34}O_2N_{12}S_4$	794	54.33 (54.41	4.17 (4.28)	21.06 (21.16)
$[V]_4$	$C_{38}H_{38}O_2N_{12}S_4$	822	55.41 (55.47)	4.54 (4.62)	20.36 (20.44)
$[V]_5$	$C_{40}H_{42}O_2N_{12}S_4$	850	56.38 (56.47)	4.99 (4.94)	19.65 (19.76)
$[X]_1$	$C_{20}H_{18}O_2N_6S_2$	438	54.65 (54.79)	4.01 (4.11)	20.75 (21.18)
$[X]_2$	$C_{22}H_{22}O_2N_6S_2$	466	56.50 (56.65)	4.51 (4.72)	17.99 (18.03)
$[X]_3$	$C_{24}H_{26}O_2N_6S_2$	494	58.17 (58.30)	5.29 (5.26)	17.00 (16.89)
$[X]_4$	$C_{26}H_{30}O_2N_6S_2$	522	59.69 (59.77)	5.67 (5.75)	16.02 (16.09)
$[X]_5$	$C_{28}H_{34}O_2N_6S_2$	550	61.02 (61.09)	6.11 (6.18)	15.20 (15.72)



(5)

In this work, the nonlinear molecules series $[V]_n$ are prepared from 1,4-bis(3-mercapto-1,2,4-triazole-5-yl)phenyl [II]. These new compounds $[V]_n$ are examples of the continuing effort to explore the limits of molecular shapes compatible with liquid crystallinity, and differ from the above reported nonlinear mesogens by the directional sense of the 2,5-substituted 1,2,4-triazole linkage in addition to 1,3,4-thiadiazole heterocyclic ring.



[II]

The mesomorphic behavior of all compounds of the two series was investigated using differential scanning calorimetry (DSC) and hot-stage polarizing optical microscopy (POM).

Table 2 collects the transition temperatures obtained by (DSC) and verified by (POM) for all ten compounds of series $[V]_n$ and $[X]_n$. Figure 1 shows the DSC thermogram of compound $[V]_4$ as representative example of these compounds. All five compounds of series were they examined under POM showed anisotropic fluid after melting. On cooling from the isotropic melt, schlieren texture characteristic of the nematic phase was observed as shown in Figure 2.

The optical and thermal data of the compounds of series $[X]_n$ are gathered in Table 2. All compounds show mesomorphic properties. Contrary to this, the compounds with two carbon atoms of terminal alkoxy group do not show mesomorphic behavior, and only crystal to isotropic liquid transition was observed. Probably, this is due to a loss of linearity in the molecules by the presence of two different heterocyclic rings which are not compatible with the even number of carbon atoms of the terminal group, for it is unable to make co-linear distribution bonding. However, the conformational caugch structure arises from the two carbon atoms of the ethoxy terminal group could be the only reason for diminishing the mesomorphity. Compounds $[X]_1$ and

TABLE 2 Phase Behavior for Compounds of Series $[V]_n$ and $[X]_n$

Compound	Phase behavior
$[V]_1$	$\mathrm{Cr}\xrightleftharpoons{190}\mathrm{N}\xrightleftharpoons{216}\mathrm{I}$
$[V]_2$	$\mathrm{Cr}\xrightleftharpoons{197}\mathrm{N}\xrightleftharpoons{250}\mathrm{I}$
$[V]_3$	$\mathrm{Cr}\xrightleftharpoons{135}\mathrm{N}\xrightleftharpoons{257}\mathrm{I}$
$[V]_4$	$\mathrm{Cr}\xrightleftharpoons{130}\mathrm{N}\xrightleftharpoons{180}\mathrm{I}$
$[V]_5$	$\mathrm{Cr}\xrightleftharpoons{105}\mathrm{N}\xrightleftharpoons{195}\mathrm{I}$
$[X]_1$	$\mathrm{Cr}\xrightleftharpoons{117}\mathrm{N}\xrightleftharpoons{202}\mathrm{I}$
$[X]_2$	$\mathrm{Cr}\xrightleftharpoons{192}\mathrm{I}$
$[X]_3$	$\begin{tikzcd} \mathrm{Cr} \arrow[r, shift left, "152"] & \mathrm{N} \arrow[l, shift left] \arrow[r, shift left, "255"] & \mathrm{I} \arrow[l, shift left] \arrow[dl, "143"] \\ & \mathrm{SmA} \arrow[ul] & \end{tikzcd}$
$[X]_4$	$\begin{tikzcd} \mathrm{Gm} \arrow[rr, shift left, "167"] & & \mathrm{I} \arrow[ll, shift left] \arrow[dl, "125"] \\ & \mathrm{SmA} \arrow[ul] & \end{tikzcd}$
$[X]_5$	$\begin{tikzcd} \mathrm{Gm} \arrow[rr, shift left, "161"] & & \mathrm{I} \arrow[ll, shift left] \arrow[dl, "97"] \\ & \mathrm{SmA} \arrow[ul] & \end{tikzcd}$

n represents the number of carbons in the alkoxy chain; Cr = crystal phase; Gm = gummy; N = nematic phase; SmA = smectic phase; I = isotropic liquid. The transition temperatures (°C).

$[X]_3$ to $[X]_5$ displayed the liquid crystalline properties. In the compound $[X]_1$ only enantiotropic nematic mesophase was observed, while compound $[X]_3$ displayed enantiotropic nematic phase on heating and monotropic smectic A (SmA) on cooling. Compounds $[X]_4$ and $[X]_5$ exhibit monotropic SmA phase. Figure 3 shows the DSC thermogram of compound $[X]_3$, the endotherms at 152°C and 255°C as examined by POM are assigned to the crystal → nematic and nematic → isotropic transitions, while the exotherms at 143°C are assigned to the

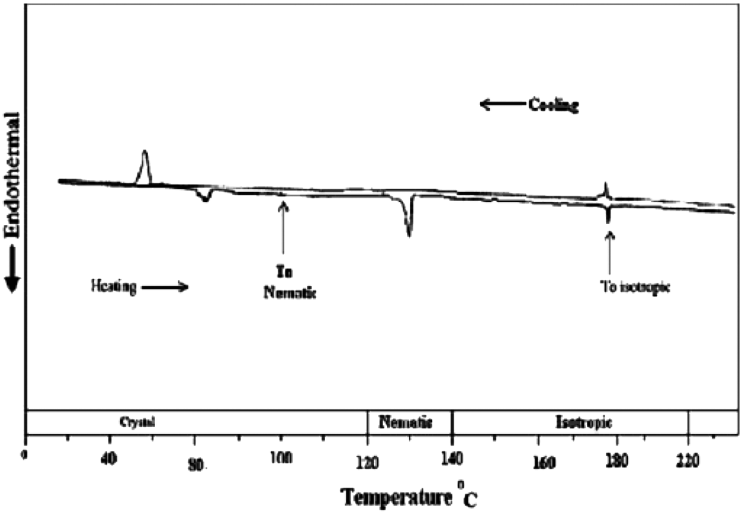


FIGURE 1 DSC thermogram for the compound $[V]_4$.

isotropic → smectic A transition. Figure 4 shows typical focal conic SmA texture of $[X]_3$. We believe that the bend imposed by the 1,2,4-triazole ring is so large that the effective polar packing necessary to build up a mesophase and neutralize the bending imposed by 1,3,4-thiadiazole ring, but with odd number of alkoxy terminal groups.

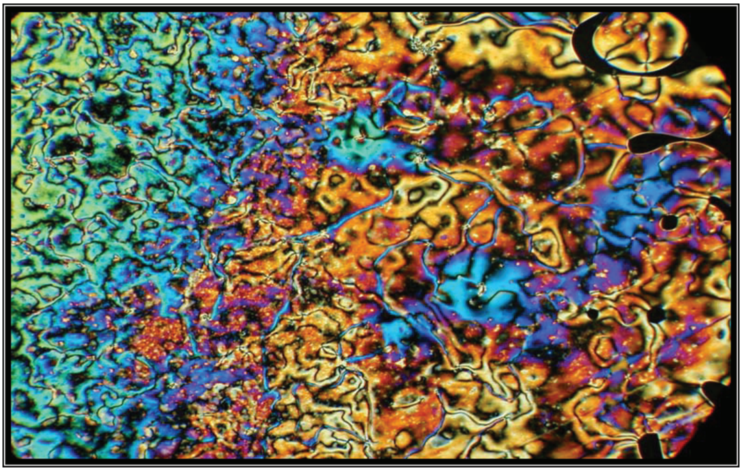


FIGURE 2 Polarizing micrograph of schlieren texture of the nematic phase (×200 magnification) of compound $[V]_5$ at 125°C on cooling.

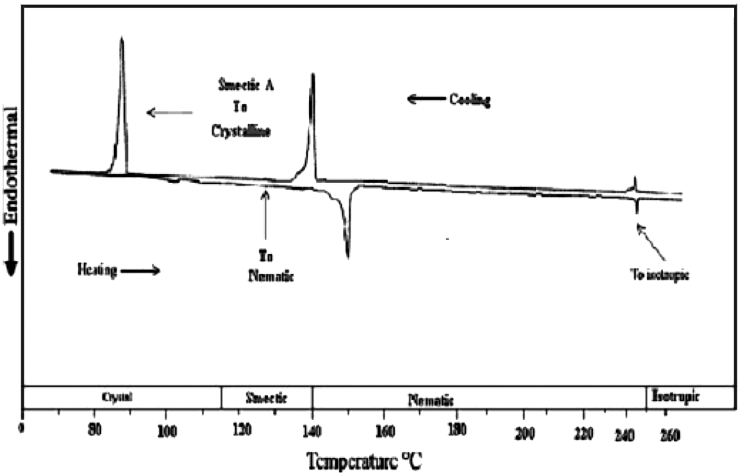


FIGURE 3 DSC thermogram for the compound $[X]_3$.

It is well known that the introduction of heteroatom causes considerable changes in chemical and physical properties and influence the type of liquid crystalline phase, also phase transition temperatures and other properties of the mesogens [8]. In our present study, we prepared two new series $[V]_n$ and $[X]_n$ containing two heterocyclic rings; one is 1,2,4-triazole and the second is 1,3,4-thiazole. The isotropic temperature of compounds in series $[V]_n$ are higher than the

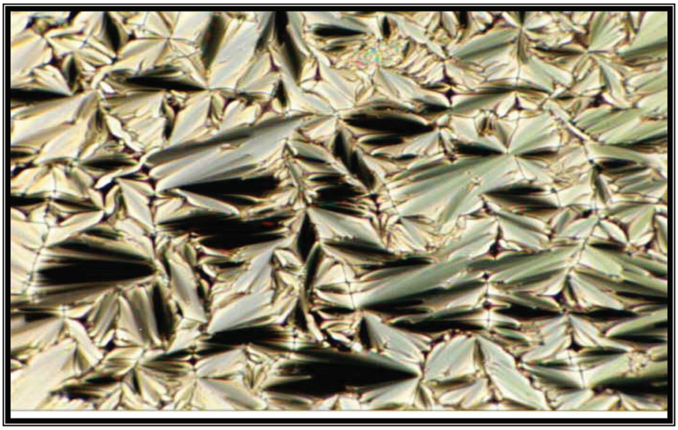


FIGURE 4 Polarizing micrograph of the focal conic texture of the smectic A phase (×200 magnification) for the compound $[X]_3$ at 125°C on cooling.

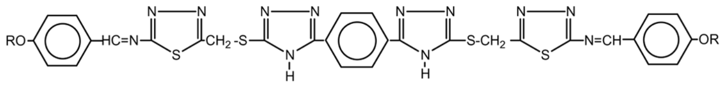
TABLE 3 Different Transition Temperatures and Mesophase Stability Range

Compound	SmA	N	I	SmA-N mesophase stability (°C)	N-I mesophase stability (°C)
$[V]_3$		135	257		122
$[X]_3$	(143)	152	255	09	103

compounds of series $[X]_n$, which is probably due to the fact that compounds of series $[V]_n$ represented the twin of compounds of series $[X]_n$. The twin compound was proved to induce boomerang shape favor of more stable liquid crystalline phases.

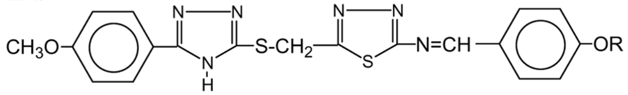
Table 3 shows the comparison of mesophases transition temperatures of compound $[V]_3$ and structurally related compound $[X]_3$. The nematic-isotropic mesophase stability of compound $[V]_3$ is higher by 19°C, when compared with compound $[X]_3$. Moreover, compound $[X]_3$ showed dimorphism enantiotropic nematic and monotropic SmA phases when compared with compound $[V]_3$. Compound $[X]_3$ is shorter than $[V]_3$, and this could increase the close packing of the former leads to more lateral molecular interaction, which is favored of smectic phase formation.

In order to show the different possibilities that 1,2,4-triazole ring can offer in the liquid crystal field, it is interesting to compare the present homologous series $[V]_n$ and $[X]_n$ with twin Schiff basses (6) prepared by us [25] and analogous Schiff's basses (7) prepared by Parra et al. [26], respectively.



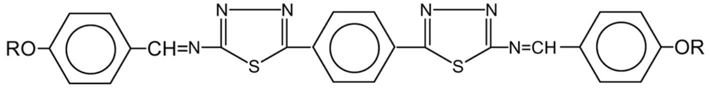
$[V]_n$

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



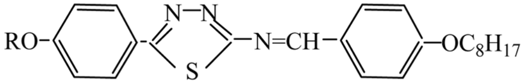
$[X]_n$

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



(6)

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



(7)

$R=C_nH_{2n+1}$, n=5-10

Series $[V]_n$ is compared with related series (6). The Schiff's bases $[V]_n$ and (6) have the same central core and the same alkoxy chains; however, the only differences between their central linkages is the 1,2,4-triazole ring. All the members of series (6) exhibit an enantiotropic dimorphism SmA-nematic, (Table 4), except the first two homologues, whereas, in series $[V]_n$ all homologues exhibit enantiotropic nematic phase. Thermal stabilities of series (6) is greater than compounds of series $[V]_n$. The flexibility and bending characters of 1,2,4-triazole could be the reason of such behavior.

Comparison of series $[X]_n$ with series (7) (despite of different chain length of alkoxy terminal substituent) give insight on the role played by the introduction of the 1,2,4-triazole ring. The structural difference between the series is one of the central linkages. All compounds of series $[X]_n$ are exhibited an enantiotropic nematic phase. The smectic SmA mesophase commences from $[X]_3$ to $[X]_5$ derivatives as a monotropic phase (Table 2), whereas all compounds of series (7) display an enantiotropic dimorphism SmC-nematic (Table 5). Thermal stabilities of compounds of series (7) is greater than compounds of series $[X]_n$. This probably can be explained considering the flexibility and bending properties of 1,2,4-triazole ring in the liquid crystalline phases. Conte et al. [28] reported that introduction of the 1,2,3-triazole in central linkages in the mesogenic molecules resulted in it showing the SmA phase, and lowered the melting point in comparison with compounds containing the only 1,3,4-thiadiazole ring in the central linkage of the molecules.

TABLE 4 Phase Behavior for Compounds of Series (6)

Compound	Phase behavior
(6) n = 1	$\mathrm{Cr} \xrightleftharpoons{>350} \mathrm{I_d}$
(6) n = 2	$\mathrm{Cr} \xrightleftharpoons{134} \mathrm{Cr_1} \xrightleftharpoons{>350} \mathrm{I}$
(6) n = 3	$\mathrm{Cr} \xrightleftharpoons{100} \mathrm{SmA} \xrightleftharpoons{235} \mathrm{N} \xrightleftharpoons{335} \mathrm{I}$
(6) n = 4	$\mathrm{Cr} \xrightleftharpoons{110} \mathrm{SmA} \xrightleftharpoons{210} \mathrm{N} \xrightleftharpoons{292} \mathrm{I}$
(6) n = 5	$\mathrm{Cr} \xrightleftharpoons{110} \mathrm{SmA} \xrightleftharpoons{200} \mathrm{N} \xrightleftharpoons{218} \mathrm{I}$

TABLE 5 Phase Behavior for Compounds of Series (7)

Compound	Phase behavior
(7) n = 5	$\mathrm{Cr} \overset{123.5}{\rightleftharpoons} \mathrm{SmC} \overset{175.8}{\rightleftharpoons} \mathrm{N} \overset{209.8}{\rightleftharpoons} \mathrm{I}$
(7) n = 6	$\mathrm{Cr} \overset{116.1}{\rightleftharpoons} \mathrm{SmC} \overset{184.3}{\rightleftharpoons} \mathrm{N} \overset{208.7}{\rightleftharpoons} \mathrm{I}$
(7) n = 7	$\mathrm{Cr} \overset{112.8}{\rightleftharpoons} \mathrm{SmC} \overset{189.5}{\rightleftharpoons} \mathrm{N} \overset{206.3}{\rightleftharpoons} \mathrm{I}$
(7) n = 8	$\mathrm{Cr} \overset{107.8}{\rightleftharpoons} \mathrm{SmC} \overset{193.9}{\rightleftharpoons} \mathrm{N} \overset{201.1}{\rightleftharpoons} \mathrm{I}$
(7) n = 9	$\mathrm{Cr} \overset{103.3}{\rightleftharpoons} \mathrm{SmC} \overset{193.9}{\rightleftharpoons} \mathrm{N} \overset{198.8}{\rightleftharpoons} \mathrm{I}$

From previous studies on crystal structure by Burgiand and Dunitz [28] and on structural effect by Byron et al. [29] on the analogous Schiff bases, a non-coplanar structure for the Schiff's bases, reported by them, which pack, together in smectic layers in a juxtaposed arrangement with a cooperative rotational arrangement in the highly order smectic phase (i.e., SmB), and free rotation in the nematic or low order smectic phase (i.e., SmA). So we may assume that in the molecules of the present Schiff's bases $[X]_n$ the juxtaposed arrangement and the cooperative rotation are absent and a free rotation of the molecules must exist, this could explain the existence of the nematic and low order SmA Phases.

CONCLUSIONS

This work has described the synthesis of two new series containing two heterocyclic rings, i.e., 1,3,4-thiadiazole and 1,2,4- triazole in the same molecules. Almost all homologues of both series showed enanatiotropic mesomorphic properties. The presence of more polarized nitrogen atoms on the both heterocyclic rings might be responsible for the formation of mesomorphic properties over other molecules containing only one heterocyclic ring. It was found that the conformational molecular structure play an important role in the stability and formation of these mesophases.

AKNOWLEDGMENT

Prof. A. H. Al-Dujaili thanks the International Institute of Education (IIE), New York, USA, for the award of a fellowship at the University of Jordan.

REFERENCES

[1] Deutscher, H., Vorbradt, H., & Zaschke, H. (1981). *Z. Chem.*, *21*, 9.

[2] Sung, H. H., & Lin, H. C. (2004). *Liq. Cryst.*, *31*, 831.

[3] Vasconcelos, U. V., Dalmoline, E., & Merlo, A. A. (2005). *Org. Lett.*, *7*, 1027.

[4] Cristiano, R., Santos, D. M. P. O., & Gallardo, H. (2005). *Liq. Cryst.*, *32*, 7.

[5] Wiss, H. Z. (1980). Z. Martin-Luther-Univ., Halle Wittenberg, *Math-Naturwiss. Reihe*, *29*, 35.

[6] Aldred, M. P., Eastwood, A. J., Kelly, S. M., & Vlachos, P.. (2004). *Chem. Mater.*, *16*, 4928.

[7] Oh, C. S. (1972). *Mol. Cryst. Liq. Cryst.*, *19*, 95.

[8] Karamysheva, L. A., Kovshev, E. I., Pavluchenko, A. L., Roitman, K. V., Titov, V. V., Torgova, S. I., & Grebenkin, M. F. (1981). *Mol. Cryst. Liq. Cryst.*, *67*, 241.

[9] Boller, A., Cereghetti, M., Schadt, M., & Scherrer, H. (1977). *Mol. Crys. Liq. Cryst.*, *42*, 215.

[10] Nash, J. A., & Gray, G. W. (1974). *Mol. Cryst. Liq. Cryst.*, *25*, 299.

[11] Aguilera, C., Parra, M., & Fuentes, G. (1989). *Z. Naturforsch.*, *53b*, 367.

[12] Parra, M., Fuentes, G., Vera, V., Villouta, S. H., & Hernandez, S. (1995). *Bol. Soc. Chil. Quim.*, *40*, 455.

[13] Pelze, G., & Diele, S. (1985). *Mol. Cryst. Liq. Cryst.*, *1*, 39.

[14] Diele, S., & Pelze, G. (1989). *Mol. Cryst. Liq. Cryst.*, *173*, 113.

[15] Li, W., Su, J., Ke, Y., & Lai, C. (2001). *J. Mater. Chem.*, *11*, 1765.

[16] Cristiano, R., Santos, D. M. P. O., Conte, G., & Gallardo, H. (2006). *Liq. Cryst.*, *33*, 997.

[17] Thaker, B. T., & Patel, P. (2008). *Mol. Cryst. Liq. Cryst.*, *482*, 3.

[18] Parra, M., Villouta, S. H., Vera, V., Belmar, J., Zuniga, C., & Zunza, H. (1997). *Z. Naturforsch*, *52b*, 1533.

[19] Parra, M., Alderete, J., Zunniga, Z., Gallardo, H., Hidalgo, P., Vergara, J., & Herna, S. (2001). *Liquid Crystal*, *28*, 1659.

[20] Shafiee, A., Naimi, E., Mansobi, P., Foroumad, A., & Shekari, M. (1995). *J. Heterocyclic Chem.*, *32*, 1235.

[21] Zamani, K., Faghiha, K., Reza, M., & Zolgharnein, J. (2003). *Turk. J. Chem.*, *27*, 119.

[22] Markess, D. J. (1989). *J. Heterocycl. Chem.*, *26*, 29.

[23] Vorlander, D., & Apel, A. (1932). *Ber.*, *65*, 1101.

[24] Dingemans, T. J., & Samulski, E. T. (2000). *Liq. Cryst.*, *27*, 131.

[25] Rou'il, I. H. (2007). Ph.D. thesis, Department of Chemistry, College of Education Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq, to be published.

[26] Parra, M., Belmar, J., Villouta, S.H., Martinez, R., Zuniga, C., & Zunza, H. (1995). *Bol. Soc. Chil. Quim.*, *40*, 175.

[27] Conte, G., Ely, F., & Gallardo, H. (2005). *Liq. Cryst.*, *32*, 1213.

[28] Burgi, H. B., & Duntz, J. D. (1970). *Helv. Chim. Acta*, *53*, 1747.

[29] Byron, D. J., Keating, D. A., O'Nell, M. T., Wilson, R. C., Goodby, G. W., & Gray, G. W. (1980). *Mol. Cryst. Liq. Cryst.*, *58*, 179.