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Synthesis and Characterization of Liquid Crystalline Behaviour of New Materials Incorporating Two Heterocyclic 1,3,4-Oxadiazole and 1,3,4-Thiadiazole Rings

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Abstract

The synthesis and mesomorphic properties of 5-(4-methoxyphenyl)-2-[2-(4'-n-alkoxy)-1,3,4-thiadiazole-5-methylenethio]-1,3,4-oxadiazole (series $[VI]_n$), were described for the number of the carbon atoms in alkoxy chains varying from 1-8. In addition, four compounds containing 4'-chloro $[VI]_a$, 4'-nitro $[VI]_b$, 4'-methoxate $[VIII]_1$ and 4'-heptoxate $[VIII]_7$ instead of 4'-alkoxy group were also synthesized to study the effect of terminal substituent. All compounds have been characterized by elemental analysis, and FTIR, mass ^{1}HNMR spectrometry. The liquid crystalline properties were investigated by differential scanning calorimetry (DSC) and optical polarized microscopy (OPM). The homologous with n=2-4 show enantiotropicnematicmesophase. The higher homologous (n = 5-8) and compound with 4'-heptaloxate $[VIII]_7$ substituent show enantiotropicnematic and smectic phases. Finally, the three compounds 4'-chloro $[VI]_a$, 4'-nitro $[VI]_b$, and 4'-metoxate $[VIII]_1$ did not show any mesomorphic properties.

الخلاصة

لقد تم تحضير ودراسة الخواص البلورية السائلة للسلسلة 5-(4-methoxyphenyl)-2-)[2-(4'-n-alkoxy)-1,3,4-thiadiazole-5-methylenethio]-1,3,4-oxadiazole (series $[VI]_n$ وبمعوضات الكوكسية فيها ذرات الكاربون من(1-8). اضافة لذلك تم تحضير اربع مركبات وهي 4-كلورو $[VI]_a$ و 4-نايترو $[VI]_b$ والاستر الميثوكسويت $[VIII]_1$ والاستر الهبتوكسويت $[VIII]_7$. تم تشخيص بعض هذه المركبات باستخدام التحليل الدقيق للعناصر ومطياف الكتلة (MS) وبروتون الرنين النووي المغناطيسي (^{1}H-NMR) كما وتم تشخيصها جميعا باستخدام مطيافية الاشعة فوق الحمراء عالية الاداء (FTIR).

شخصت الخواص البلورية السائلة بأستخدام مسعر المسح التفاضلي (DSC) والمجهر ذي الضوء المستقطب المزود بمنصة تسخين (OPM). لقد أظهرت مركبات السلسلة (VI)n مع (n=2-4) خواص بلورية سائلة نيماتية بينما أظهرت مركبات السلسلة (n=5-8) اضافة الى المركب 4-هبتولوكسي خواص بلورية سائلة متعددة الاطوار النيماتية والسمكتية. بينما لم تظهر المركبات $[VI]_1$ $[VIII]_1$ $[VIII]_7$ أي خواص بلورية سائلة وانما انتقلت من الطور البلوري الى الطور الايزوتروبي مباشرة.

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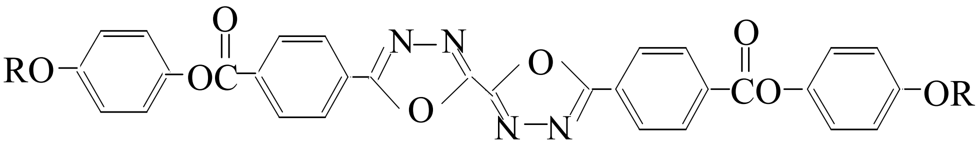
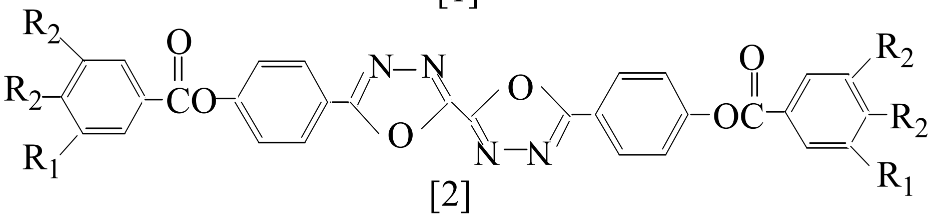
Introduction

During the last decades a large number of liquid crystalline compounds containing heterocyclic units have been synthesized (1-7). 1,3,4-Oxadiazole and 1,3,4-thiadiazole derivatives , a type of five membered heterocyclic compounds consisting of nitrogen and oxygen or sulfur atoms, are one of the most widely investigated classes (8-16). Recently Zhang et al.(17, 18) synthesis and studied symmetrical bi-1,3,4-oxadiazole derivatives [1] and [2] respectively, whichwere exhibited smecticC phase liquid crystalline behaviour.



[1]



[2]

The goal of this work was the synthesis and study liquid crystallinebehaviour of new design of novel thermotropic liquid crystalline compounds containing two types of heterocyclicring in the same molecule namely, 1,3,4-oxadiazole and 1,3,4-thiadiazol rings with SCH_2bridge.

Experimental

MATERIALS : Most of chemicals used were supplied from Flukaand Aldrich Chemicals, and were used without further purification .

Instruments: Uncorrected melting points were determined by using an Electro thermal melting point apparatus. FTIR spectra were recorded on a 8400S Shimadzu Spectrophotometer by using potassium bromide disc. ^{1}H-NMR spectra were obtained with a Varian Mercury plus spectrometer 400 MHz instrument using suitable duterated solvent and TMS as internal standard.The optical behavior observations were made using Olympus BX40 microscope equipped with a LeitzLaborlux 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 of Compounds

Preparation of n-alkylbromide, carboxylic acid chlorides,methyl-4-methoxy benzoate[I] and4-n-alkoxybenzaldehyde were preparedaccording to references (19,20).4-Methoxyphenylhydrazide [II] and 5-(4-methoxyphenyl)-1,3,4-oxadiazole-2-thiol[III] were prepared according to procedure previously described in our previous work(21) .

The new compounds were synthesized according to Scheme 1 by the following general procedure.

5-(4-Methoxyphenyl)-2-thioaceticacid 1,3,4-oxadiazole[IV]

To a stirring of α-chloro acetic acid (0.01mol) in 10% aqueous sodium hydroxide (10 mL), a solution of oxadiazole [III] (0.01mol) in 10% aqueous solution of sodium hydroxide (10 mL) was added, the mixture was refluxed for 3hrs. After cooling, the solution was acidified with concentrated hydrochloric acid(22). The precipitate was filtered and recrystallized from ethanol to yield pale yellow solid 82%, m.p=160-163°C.

FTIR (KBr disc , cm^{-1}) ν : 2750-3298 (OH of CO_2H) ; 2960 (CH aliph.) ; 1685 (C=O of carboxylic moeity) ; 1616 (C=N in oxadiazole ring) ; 1595 (C=C benzene ring) ; 1255 (CO , ether) ; 840 of bending para substituted benzene ring .MS: m/z= 266.

5-(4-Methoxyphenyl)-2-(2-amino-1,3,4-thiadiazole-5-methylenethio)-1,3,4-oxadiazole[V]

A mixture of compound [IV] (0.01mol), thiosemicarbazide (0.01mol), phosphorusoxychloride(10 mL)was refluxed gently for 48 hs. After cooling, ice water (50 mL) was added in portions with stirring. The yellow precipitate was filtered, washed with hot water(23), recrystallized from ethanol, yield 60% ,m.p196-198°C.

FTIR (KBrdisc , cm^{-1}) ν : two peaks at 3213 and 3100 (NH_2 , asym.and sym.); 2839-2935 (CH aliph.) ;two peaks around 1615 and 1606 (C=N in oxadiazole and thiadiazole rings) and 835 of bending para substituted benzene ring.

^{1}HNMR (DMSO ,ppm) δ : 7.9-9.9(d-d , 4H , aromatic proton);6.4(broad s, 2H , NH_2); 6.0 (s, 2H , SCH_2);4.6 (s , 3H , OCH_3).

5-(4-Methoxyphenyl)-2-[2-(4'-substituted or hydroxybenzelidene-amino)-1,3,4-thiadiazole-5-methylenethio]1,3,4-oxadiazole [VI]$_{a,b,n}$ and [VII]

A mixture of compound[III] (0.001mol) , 4-substitutedbenzaldehyde (0.012 mol), ethanol absolute (10mL) and 3drops of glacial acetic acid was refluxed for 5 hs. After cooling the precipitate solid was filtered and recrystallized using chloroform.

Calc. for compounds [VI]$_1$, $C_{20}H_{17}O_2N_5S_2$, C%, 54.67; H%, 3.87; N%, 15.95; Found: C%, 54.65; H%, 4.01; N%, 15.75. MS:m/z+1 = 440.

FTIR (KBr disc, cm^{-1}) ν : 3003-3076(CH aromatic) ; 2837-2958 (CH aliph.); 1640 (C=N , imin group); 1259 (CO , ether); 831 of bending para substituted benzene ring

^{1}HNMR (DMSO , ppm) δ : 9.8 (s , 1H , CH=N) ; 7.7-7.9 (d-d , 4H , aromatic proton) ; 6.9-7.1(m, 4H aromatic , N=CHPh) ; 3.6 (s, 2H , SCH_2) ; 2.6 (s , 3H , OCH_3 near from oxadiazole ring) ; 2.2 (s , 3H , OCH_3 near from shiff base).

FTIR of compounds [VII] (KBr disc , cm^{-1}) ν : 3414 (OH group) ; 3093-(CH aromatic) ; 2928 (CH aliph.) ; 1650 (C=N , imin group) ; 1255-1265 (CO , ether) ; 833 of bending para substituted benzene ring .MS: m/z = 425.

5-(4-Methoxyphenyl)-2-[2-(4'-n-acyloxybenzelideneamino)-1,3,4-thiadiazole-5-methylenethio]1, 3, 4-oxadiazole [VIII]$_m$

To a stirred solution of compound[VII] (0.01mol), Et_3N (0.02) in dried mixture of (4mL DMF : 6 mL THF), was added dropwise carboxylic acid chloride (0.014mol) at (0-4)^{o}C . After the addition had been completed the mixture was stirred for 3hs at the same temperature . The reaction mixture was poured into (50mL) ice-water then the mixture was extracted by adding (50mL) of ether . The ether solution was evaporated to give a residue which was dried in air . FTIR of compounds [VIII]$_1$ (KBr disc , cm^{-1}) ν : 2852-2955 (CH aliph.) ; 1730(C=O , ester group) ; 1645 (C=N , imin group) ; 1257 (CO , ether) ; 835 of bending para substituted benzene ring.MS: m/z=467.

Results and Discussion

Synthesis and Characterization

Scheme 1 outline the synthesis of the eight compounds of series $[VI]_n$ and four compounds $[VI]_a$, $[VI]_b$, $[VIII]_1$ and $[VIII]_7$. The elemental analysis and mass and ^{1}HNMR spectroscopy of some of these compounds and FTIR spectroscopy for all synthesized compounds confirmed the structural formula and indicating structure of respective compounds.The physical data for all synthesized compounds are listed in Table 1.

Table 1: Physical data of series $[VI]_n$ and compounds $[VI]_a$, $[VI]_b$, $[VIII]_1$ and$[VIII]_7$.

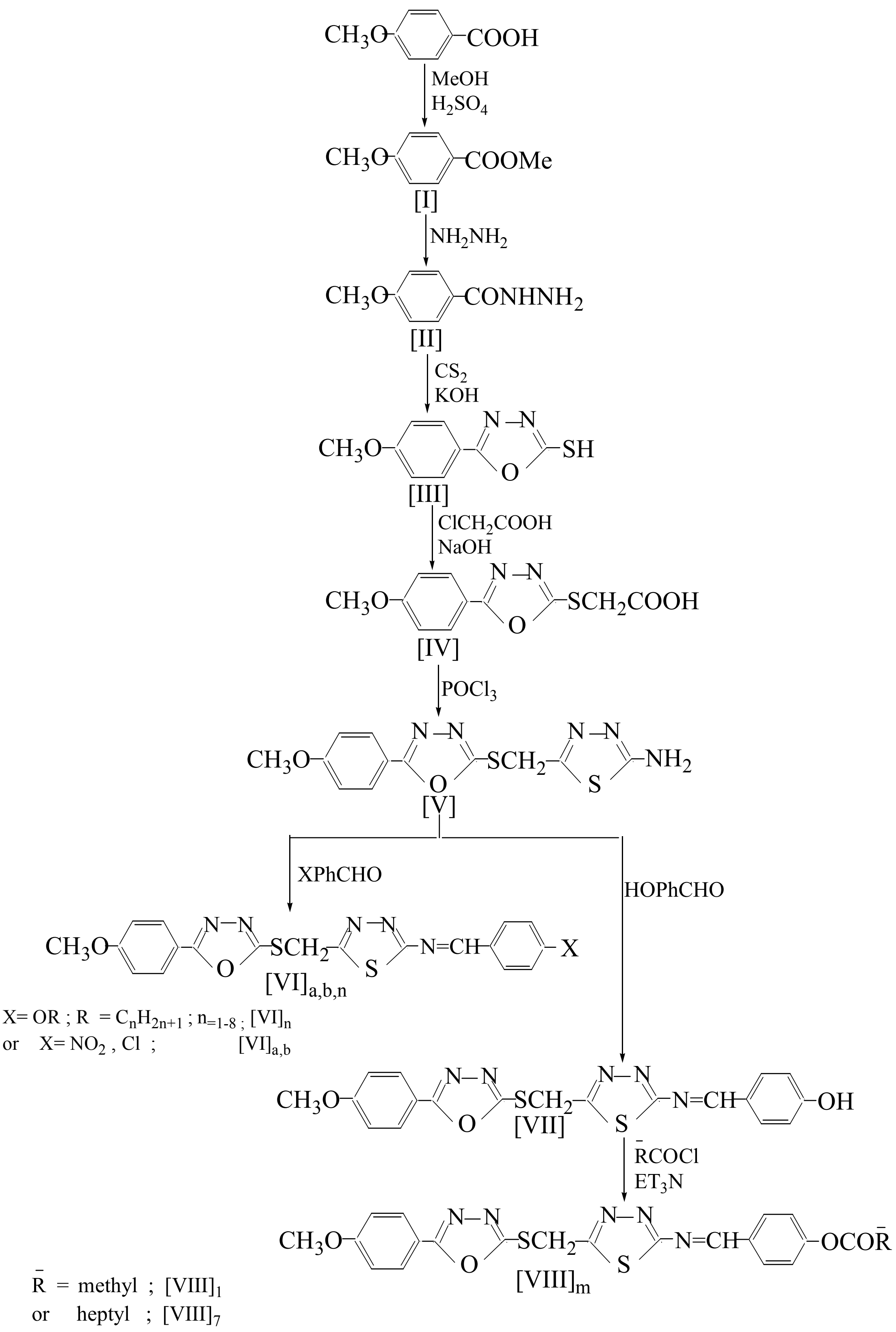
Comp. No.	X-	R^-	Formula	Yield %	Color
$[VI]_a$	NO_2	-	$C_{19}H_{14}N_6O_4S_2$	75	Orange
$[VI]_b$	Cl	-	$C_{19}H_{14}N_5O_2S_2Cl$	80	Green
$[VI]_1$	OCH_3	-	$C_{20}H_{17}N_5O_3S_2$	65	Yellow
$[VI]_2$	OC_2H_5	-	$C_{21}H_{19}N_5O_3S_2$	40	Brown
$[VI]_3$	OC_3H_7	-	$C_{22}H_{21}N_5O_3S_2$	64	Yallow
$[VI]_4$	OC_4H_9	-	$C_{23}H_{23}N_5O_3S_2$	60	Yallow
$[VI]_5$	OC_5H_{11}	-	$C_{24}H_{25}N_5O_3S_2$	40	Brown
$[VI]_6$	OC_6H_{13}	-	$C_{25}H_{27}N_5O_3S_2$	44	Brown -Yallow
$[VI]_7$	OC_7H_{15}	-	$C_{26}H_{29}N_5O_3S_2$	42	Brown -Yallow
$[VI]_8$	OC_8H_{17}	-	$C_{27}H_{31}N_5O_3S_2$	76	yellow
$[VIII]_1$	-	CH_3	$C_{21}H_{17}N_5O_4S_2$	40	Green-Brown
$[VIII]_7$	-	C_7H_{15}	$C_{28}H_{31}N_5O_4S_2$	52	Brown -Yallow

All synthesized compounds examined by differential scanning calorimeter (DSC) and verified by hot-stage optical polarizing microscopy (OPM). Table 2 collects the transition temperatures obtained by (DSC) and verified by (POM) for all eight compounds of series $[V]_n$and four compounds $[VI]_a$, $[VI]_b$, $[VIII]_1$ and $[VIII]_7$. The ethercompounds $[VI]_n$with n=2-8 and ester compound $[VIII]_7$ exhibited mesomorphicbehaviour. The compounds$[VI]_a$, $[VI]_b$, $[VI]_1$and $[VIII]_1$did not show any liquid crystalline properties but simply change from solid crystal to isotropic liquid .

The ether compounds $[VI]_n$ with n= 2-4 showed pure enantiotropicnematic phase (nematogene), All three compounds of series were they examined under POM showed anisotropic fluid after melting. The compounds $[VI]_n$ with n=5-8 and $[VI]_8$displayed enantiotropicnematic and smecticSm phases.Figure1 shows typicalfocal conicsmectic A texture of $[VI]_8$ and theSchlieren texture characteristic of the nematic phase was observed as shown in Figure 2.

Table 2: Liquid crystalline transition temperatures (^{o}C) of series $[VI]_n$ and compounds $[VI]_a$, $[VI]_b$, $[VIII]_1$ and $[VIII]_7$.

Comp. No.	Cr SmN I
$[VI]_a$	• 150 - -•
$[VI]_b$	• 168- - •
$[VI]_1$	•162.5 - -•
$[VI]_2$	•170 - •252 •
$[VI]_3$	•181 - • 269 •
$[VI]_4$	•138 - • 192 •
$[VI]_5$	•145 • 187 • 223 •
$[VI]_6$	•132 • 182 •215 •
$[VI]_7$	•147 • 185 • 238 •
$[VI]_8$	•131 •194 • 221 •
$[VII]_1$	•>300•
$[VII]_7$	• 117 •177 • 220•


CH3O–C6H4–COOH
MeOH
H2SO4
CH3O–C6H4–COOMe
[I]
NH2NH2
CH3O–C6H4–CONHNH2
[II]
CS2
KOH
N–N
SH
O
[III]
ClCH2COOH
NaOH
SCH2COOH
[IV]
POCl3
SCH2
NH2
S
[V]
XPhCHO
HOPhCHO
N=CH
X
[VI]a,b,n
X= OR ; R = CnH2n+1 ; n=1-8 ; [VI]n
or X= NO2 , Cl ; [VI]a,b
OH
[VII]
R̄COCl
ET3N
OCOR̄
[VIII]m
R̄ = methyl ; [VIII]1
or heptyl ; [VIII]7

Scheme 1

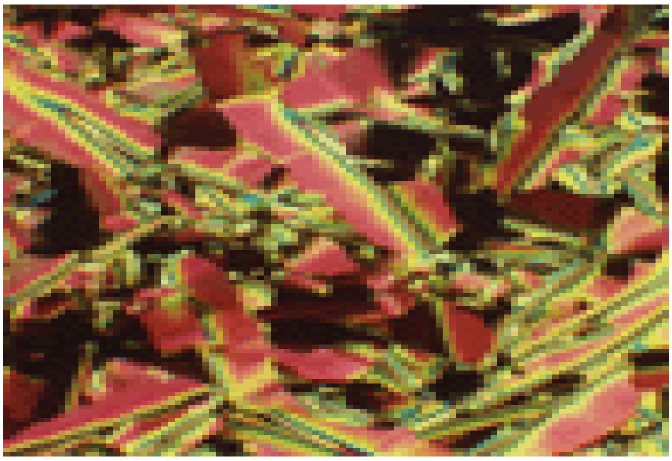


Figure 1 : Polarizing micrograph ofSmectic phaseS_A(x200 magnification) of compound [VI]$_8$ at 150 ^oC on heating.

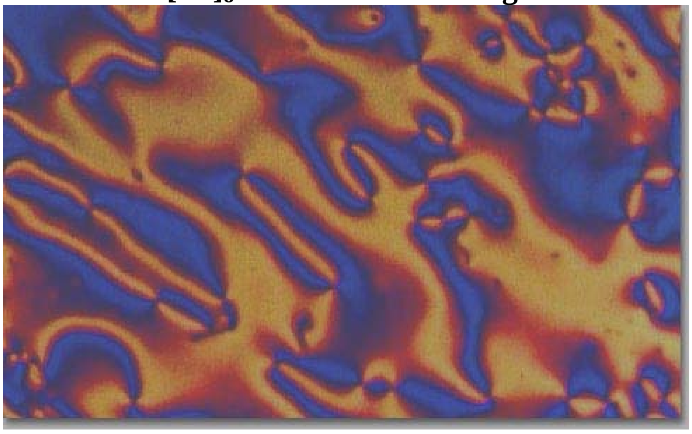


Figure 2 : Polarizing micrograph of schlieren texture of the nematicphase(x200 magnification) of compound [VI]$_8$ at 210 ^oC on heating.

Liquid Crystalline Behaviour

This behaviour of above could be explain in term of terminal /lateral (t/l) interaction forces ratio . When this ratio is high, compounds tend to give less ordered mesophases (nematicmesophase)as compounds [VI]$_{2-4}$. While this ratio is low that mean the alkyl group is now sufficiently long and thus more polarizable to overcome residual terminal cohesive forces and smectic phaseappear, as compounds [VI]$_{5-8}$ and ester compounds [VIII]$_7$. Finally, when this ratio is very high may be cause disappear the mesomorphicbehaviour as compounds [VI]$_{a,b,1}$and [VIII]$_1$(23) .

The phase transition temperatures versus the number of carbon atoms of alkyl chain (n) of compounds [VI]$_n$ are plotted in Figure 3, from this Figure one can see:

1) The usual odd-even effect of the nematic –isotropic transitions andcrystal-smectic transitions can be clearly seen from this Figure3. The liquid crystalline thermal stability of nematic phase (temperature difference temperature) is

some what wider for the odd member than for the even members. While the thermal stability of smectic phase is wider for even member thanfor the odd member .

2) The increase of (n) of alkyl group of $C_nH_{2n+1}O$- in the series $[VI]_n$ were found to play an important role in mesophase type and formation

3) All compounds [VI] with n=2-8 except n=4 shows good phase range and thermal stability, compound $[VI]_4$ exhibited low transition temperatures of the nematic to isotropic and a narrow phase range.

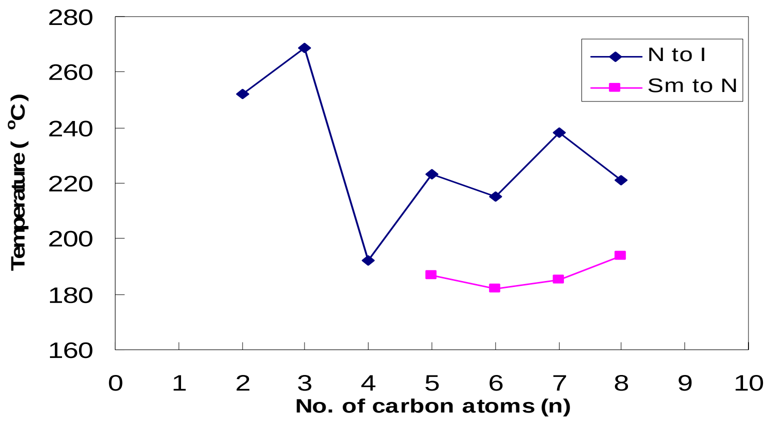
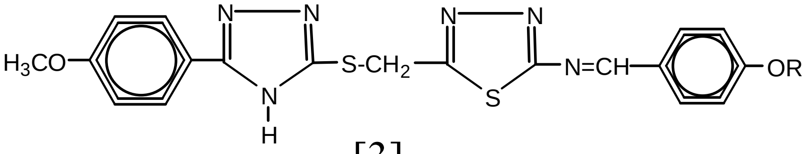


Figure 3: Plot of transition temperature against alkyl chain length (n) of series $[VI]_n$.

Acomparison of the mesomorphic properties and transition temperatures of these compounds $[VI]_n$ n=1-8 with a homologous series (24) of structural formula $[3]_n$ one can found that the later compound [3] with n=2,4 and 5 did not show any liquid crystalline properties only compounds [3] with n= 1 and 3 exhibited liquid crystalline behaviourwith a narrow range of transition temperatures and lower thermal stability . probably, the high thermal stability of our ether compounds $[VI]_n$is due to that the 1,3,4-oxadiazole core give rise to more planar and polariazble ring than the 1,2,4-triazole ring.



$[3]_n$

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

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