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THE PREPARATION AND LIQUID CRYSTALLINE PROPERTIES OF SOME HOMOLOGUES SERIES OF 1, 2, 4-OXADIAZOLE DERIVATIVES

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Abstract

Homologues series of some derivatives of 3, 5-(4-substituted phenyl)-l, 2, 4-oxadiazole were synthesized and their phase behavior was studied. Introduction of the pentagonal hetero aromatic ring leads to significant changes in mesomorphic behavior. The synthesized compounds exhibit nematic phase.

تحضير ودراسة الصفات البلورية السائلة لبعض السلاسل المتشابهة لمشتقات ١، ٢، ٤- اوكسادايازول

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الخلاصة

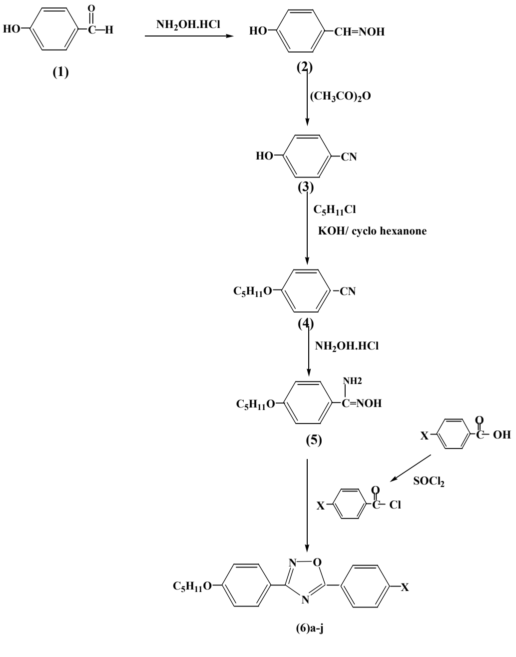
تم تحضير ودراسة الخواص البلورية السائلة لسلاسل منتشابهة لبعض مشتقات الـ ٣، ٥-(٤- فنيل معوض)- ١، ٢، ٤- اوكسادايازول. لوحظ ان وجود الحلقة الاروماتية غير المتجانسة الخماسية ادى الى تغير مهم في الخواص البلورية السائلة. اعطت المركبات المحضرة اطواراً نيماتية.

Introduction

During the last fifteen years a large number of mesomorphic compounds containing heterocyclic units have been synthesized and interest in such compounds constantly grows [1, 2]. The inclusion of hetero atoms can cause large changes in the mesomorphic behavior whether in the kind of mesophase present or in the physical properties of the phases. The well-established classical concept required for mesomorphic behavior is a molecular geometry as close to linear as possible [3]. This linearity is generally obtained using the 1, 4-disubstituted-henyl ring as the basic unit in the molecule. The incorporation of five member heterocyclic rings as units in the molecule has been taken a great attention in the last two decades [4]. However, 1, 3, 4-thiadiazoles, 1, 2, 4-thiadia-zoles and 1, 3, 4-oxadiazoles [5, 6] pentagonal heterocyclics have been studied as structural units for liquid crystals. A disubstituted pentagonal ring is not collinear and this causes a significant loss of linearity [7].
Here our objective is to study the potential and compatibility of derivatives of 1, 2, 4-oxadiazole in the generation of mesomorphic behavior.

Synthesis

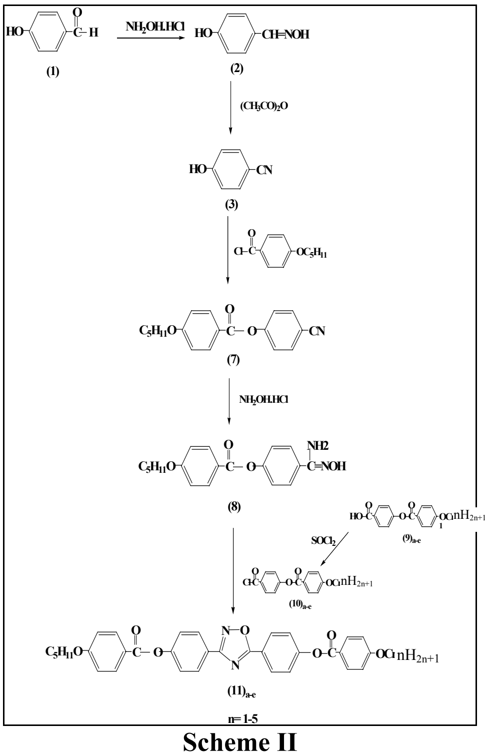
The 3, 5-diaryl- 1, 2, 4-oxadiazoles **6(a-j)** were prepared according to the synthetic route shown in scheme I. The phenolate solution obtained by the reaction of 4-hydroxybenzonitrile and potassium carbonate was treated with chloropentane to give the 4-pentoxybenzonitrile **4**. Compound **4** in ethanol was reacted with a solution of hydroxylamine hydrochloride in water, to give the 4-n-pentoxybenzamidoxime **5**. The following step is the conversion of compound **5** into the 3, 5-diaryl-1, 2, 4-oxadiazole by heating with the 4-alkoxybenzoyl chloride or corresponding derivative of the carboxylic acids. The solvent in this reaction is pyridine which plays the role of an acceptor for HCl [1].



x = $-OC_nH_{2n+1}$ (n = 1-5), F, Cl, Br, I and NO_2

Scheme I

The reaction pathway used to prepare the 3- (4-pentoxy benzoyloxyphenyl)-5-(4′-alkoxybenzoyloxyphenyl)-1, 2, 4-oxadiazole $\mathbf{(11)}_{a-e}$ is shown in scheme II.



Scheme II

The amidoxime **8** and oxadiazoles $\mathbf{(11)}_{a-e}$ were prepared using the same method described in scheme I.

Results and Discussion

3- (4 -pentoxyphenyl) - 5- (4′- substitutedphenyl)-l, 2, 4-oxadiazole. Table (1) summarizes the mesomorphic behavior of the series **6(a- j)** with various chain lengths and substituents.

Table 1: Melting points and Transition temperatures obtained from hot-stage polarizing microscopy of the compounds 6(a- j)

Comp. No.	**X-**group	Transition	t °C	t °C Hot stage
$\mathbf{(6)_a}$	$\mathbf{-OCH_3}$	C → I	125-127	-
$\mathbf{(6)_b}$	$\mathbf{-OC_2H_5}$	C → I	118-122	-
$\mathbf{(6)_c}$	$\mathbf{-OC_3H_7}$	C → N C → I	127-133	126.6 132.2
$\mathbf{(6)_d}$	$\mathbf{-OC_4H_9}$	C → N C → I	106-112	104.7 110.4
$\mathbf{(6)_e}$	$\mathbf{-OC_5H_{11}}$	C → N C → I	100-118	101.2 106.2
$\mathbf{(6)_f}$	**-F**	C → I	130-135	-
$\mathbf{(6)_g}$	**-Cl**	C → N C → I	136-141	135.5 140.6
$\mathbf{(6)_h}$	**-Br**	C → N C → I	148-154	147.8 151.3
$\mathbf{(6)_i}$	**-I**	C → I	160-162	-
$\mathbf{(6)_j}$	$\mathbf{-NO_2}$	C → S_A S_A → N N → I	146-156	148.4 148.9 154.7

As can be observed in Table (1), the melting point decreases slightly with increase in the chain length. Microscopic observations of compounds of $\mathbf{(6)_{a-e}}$ at liquid crystalline transition temperature displayed a nematic mesophase of typical nematic droplets are observed on cooling from the isotropic liquid for compounds $\mathbf{(6)_{c,d,e}}$, (Figures 1-3), while compounds $\mathbf{(6)_{a,b}}$ did not show any liquid crystal properties. The absence of mesomorphicity of compound $\mathbf{6_{a,b}}$ might be due to the length of alkoxy group which is less than half the length of the molecules. Herbert [8] found that mesophase formation ability starts when the alkyl chain is almost half the length of the whole molecule.

Compounds $(\mathbf{6})_f$ and $(\mathbf{6})_i$ did not show any mesomorphic properties, while compounds $(6)_{g,h}$ show a nematic droplets mesophase, (Figures 4 and 5).

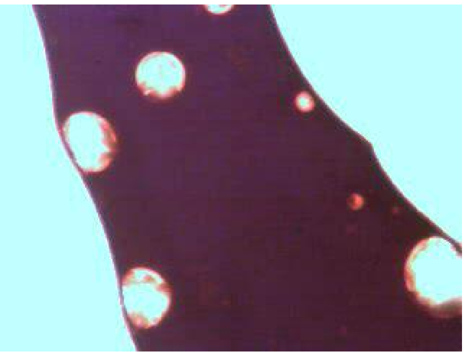


Figure 1: Nematic texture of compound $(6)_c$ at 130°C.

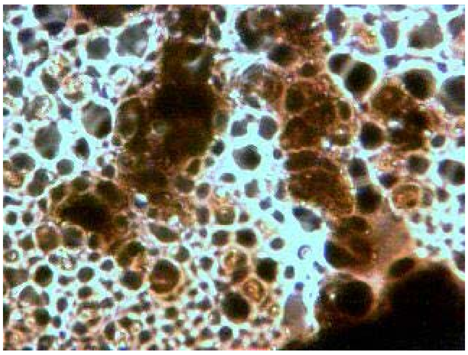


Figure 2: Nematic texture of compound $(6)_c$ at 107°C.

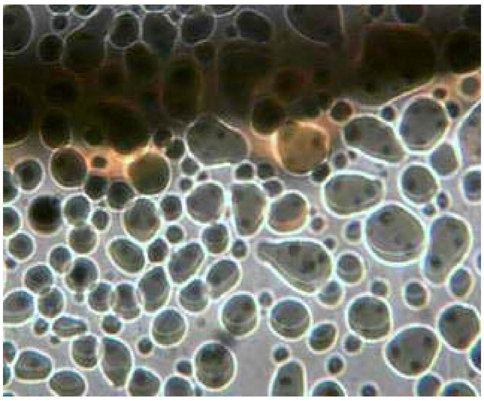


Figure 3: Nematic texture of compound $(6)_c$ at 104°C.

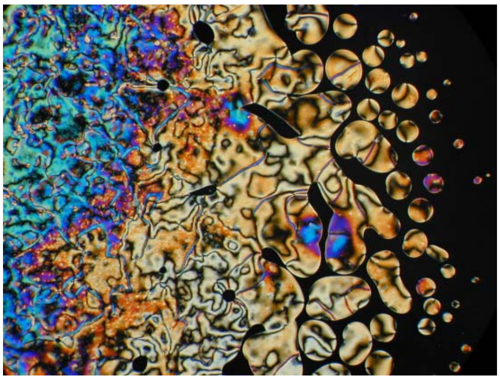


Figure 4: Nematic droplet texture of $(6)_h$ at 149°C.

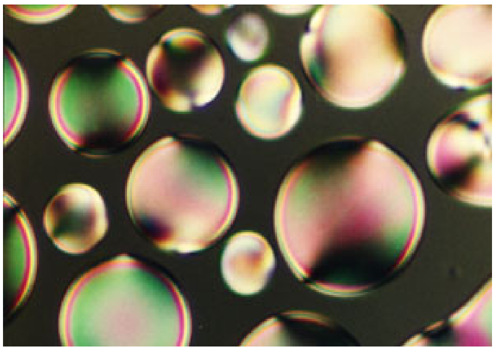


Figure 5: Nematic texture of compound $(6)_g$ at 137°C.

Compound $(\mathbf{6})_j$ shows monotropic smectic A and nematic phases, (Figure 6). The presence of the smectic A phase in this compound can be explained in terms of non-linear geometry and conjugate effects. The lone pair of the oxygen in the heterocyclic ring may conjugate with the nitro group and thereby set-up a permanent dipole, which has a substantial component directed laterally. This would increase the lateral intermolecular cohesive force, and the tendency to form a smectic mesophase [8].

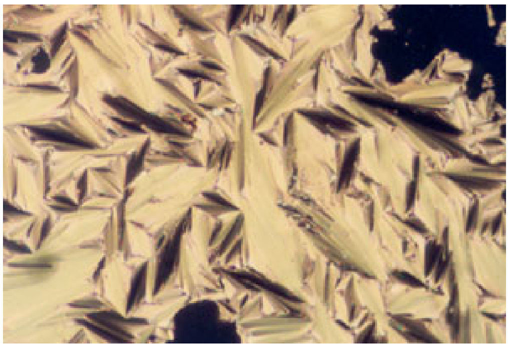


Figure 6: Smectic A texture of compound $(6)_j$ at 150° C.

The tendency of a compound to show one type of mesophase or another is determined by linearity, rigidity, polarizability and by the direction of dipole moment (perpendicular or oblique to the molecular axis). These properties are indispensable for displaying liquid crystallinity [14].

Liquid crystalline properties of compounds $(\mathbf{11})_{a-e}$ was examined by means of hot stage optical polarizing microscope. Table (2) summarizes the mesomorphic behavior of the series $(\mathbf{11})_{a-e}$ with various chain length. Compounds $(\mathbf{11})_{a-e}$ showed a nematic mesophase of a typical thread- like texture as shown in (Figures 7 – 11).

It is well known that the type of mesophase (smectic or nematic) is determined mainly by the intermolecular attractions which operate between the sides and planes of the molecules, i.e., the strengths of the lateral and terminal attraction forces [9].

Table 2: Melting points and Transition temperatures obtained from hot-stage microscopy of the compounds $(11)_{a\text{-}e}$

Comp. No.	X-group	Transition	t °C	t °C Hot stage
$\mathbf{(11)_a}$	$\mathbf{-OCH_3}$	$C \longrightarrow N$ $C \longrightarrow I$	223-235	220 233
$\mathbf{(11)_b}$	$\mathbf{-OC_2H_5}$	$C \longrightarrow N$ $C \longrightarrow I$	200-209	198 211
$\mathbf{(11)_c}$	$\mathbf{-OC_3H_7}$	$C \longrightarrow N$ $C \longrightarrow I$	197-207	195 205
$\mathbf{(11)_d}$	$\mathbf{-OC_4H_9}$	$C \longrightarrow N$ $C \longrightarrow I$	182-191	180 193
$\mathbf{(11)_e}$	$\mathbf{-OC_5H_{11}}$	$C \longrightarrow N$ $C \longrightarrow I$	178-189	176 188

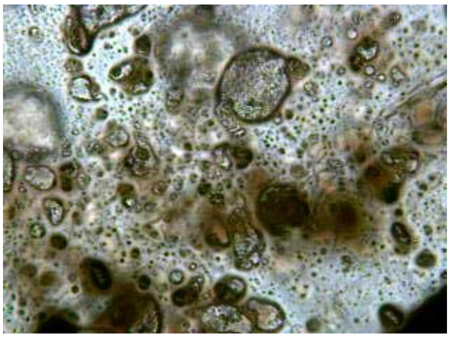


Figure 7: Nematic texture of compound $(11)_a$ at 230°C.

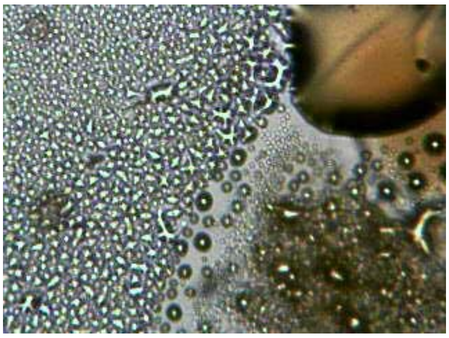


Figure 8: Nematic texture of compound $(11)_b$ at 205°C.

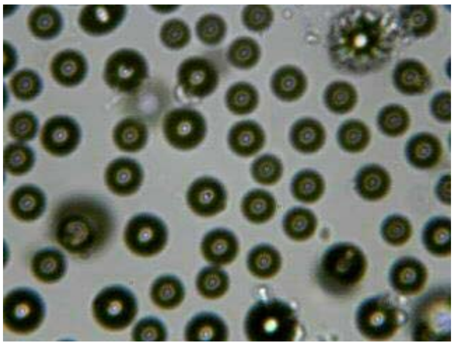


Figure 9: Nematic texture of compound $(11)_c$ at 200°C.

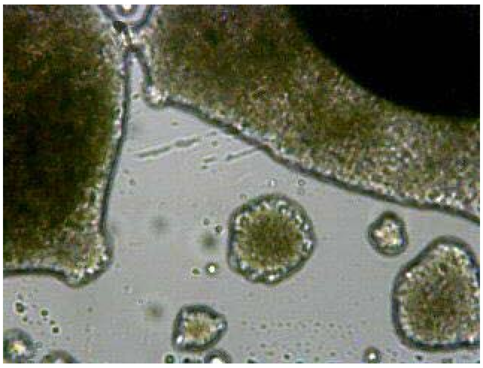


Figure 10: Nematic texture of compound $(11)_d$ at 185°C.

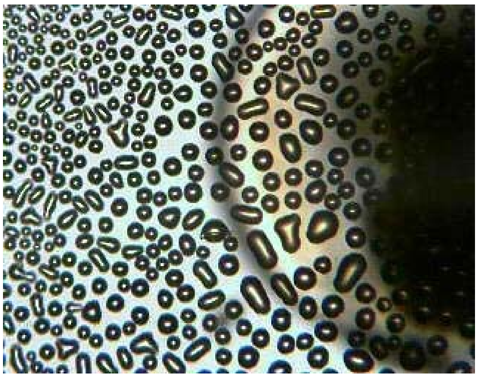
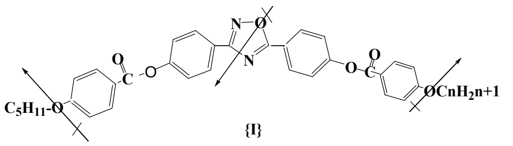


Figure 11: Nematic texture of compound $(11)_e$ at 182°C.

It appeared that a relatively small or compact group situated terminally in a molecule would enhance the nematic properties of the compound. For the oxadiazole containing compound, the lateral attractions could arise from the dipolar parts of the molecules (1), one might predict that compound $\mathbf{(11)_{a\text{-}e}}$ would be a smectic compound. In fact compound $\mathbf{(11)_{a\text{-}e}}$ is considered as purely nematic. Our prediction should of course have taken into account the two terminal pentoxy and alkoxy groups which lied high in the order of group efficiency for nematic mesophase formation, possibly by their influence on terminal intermolecular attractions.



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The oxadiazole group will cause some deviation from linearity [10]. This may make it difficult for the molecule to be assumed a layer crystal lattice conducive to smectic behavior. Also the bend in the molecular shape was reduced to a certain degree if the oxadiazole ring was shifted to the terminal position of the rigid aromatic core and the oxadiazole ring might be looked upon as a polar terminal substituents.

Experimental

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. The IR spectra were recorded using KBr disc with a *8300 shimadzu spectrometer*, and the ^{1}H NMR spectra were recorded on a *Brüker ACF 300* Spectrometer operating at 300MHz. The 4-alkoxybenzoyl chlorides were prepared by standard methods [11].

4-hydroxybenzaldoxime (2). (10 g, 0.144 mole) of hydroxyl amine hydrochloride was dissolved in (20 mL) of water and (40 mL) of 10 percent of NaOH then (4 g, 0.0327 mole) of *p*-hydroxybenaldehyde was added. The mixture was refluxed for 1hr. then was cooled in ice, and the solid product was filtered and dried. The yield of oxime (m.p. = 67-69 °C) was 90 %. FTIR (KBr disc cm^{-1}): broad band at 3379.1 that attributed to the stretching of O-H groups. Bands at 1610.5, 1517.9 and 1479.3 that are due to C=N and C=C aromatic stretching. Sharp strong band at 827.4 also observed that are assigned to out of plane bending of *p*-disubstituted benzene ring.

4-hydroxybenzonitrile (3). A mixture of (4 g, 0.033 mole) of 4-hydroxy benzaldoxime (**2**) and 10 mL of acetic anhydride was refluxed for 1hr, then poured carefully with stirring into 75 mL of cold water. Stirring was continued with cooling in ice. The formed crystals were filtered off and dried. The yield was 93% of product. FTIR (KBr disc cm^{-1}): band at 3421 which could be assigned to O-H stretching. A new stretching band appeared at 2229.5 which could be attributed to nitrile group.

4-pentoxybenzonitril (4). A mixture of 4-hydroxy benzonitrile (**3**) (3g, 0.026 mole), potassium carbonate (3.61 g, 0.0261 mole) and dry cyclohexanone (5mL) was heated at 65°C for several minutes. Then chloropentane (0.0268 mole) was added dropwise and the reaction mixture were refluxed for 24 hrs. After filtration and evaporation of the solvent the oil residue was purified by distillation under reduced pressure.

4-pentoxybenzoyloxy benzonitrile (7). A mixture of 0.002 mole of the *p*-pentoxy benzoic acid, 5 mL of $SOCl_2$, and one drop of DMF was refluxed for 2-3 hrs. The excess of the $SOCl_2$ was then distilled off. The acid chloride obtained was added to the solution of 0.2 mmole of p-hydroxy benzonitrile (**3**) in 10 ml of pyridine, cooled to 0°C, and the mixture was stirred on a magnetic stirrer at 20°C for 48 hrs. The mixture was poured into 50 ml of 10% HCI, and the precipitated residue was filtered off, washed with water, and dried.

4-substitutedbenzamidoxime (5) and (8). A solution of (0.178 mole) hydroxylamine hydrochloride was added to a sodium hydroxide solution (0.178 mole of sodium hydroxide in 10ml of water). Then the resulting mixture was added to a solution of (0.158 mole) of *p*-substituted benzonitrile in 80mL of ethanol. The mixture was refluxed for 3 hrs. After cooling in an ice bath for 2 hrs., colorless crystals were formed then filtered and dried. The crystals were recrystallized from ethanol or a mixture ethanol/water mixture.

3,5-(disubstitutdphenyl)-1,2,4-oxadiazole (6)$_{a-j}$ and (11)$_{a-e}$. 4-substituted benzamid-oxime (0.045 mmole) was dissolved in dry pyridine (15 mL). The appropriate *p*-substituted benzoyl chloride (0.047 mole) was then added drop wise. The mixture was heated under reflux for 5 hrs. The cooled reaction mixture was poured into water (100 mL). The crude product was purified by recrystallization from ethanol .Table (3) shows the melting points and % yield of the synthesized compounds. Table (4) shows the FTIR bands and ^{1}HNMR for some synthesizes compounds.

The ^{1}HNMR ($CDCl_3$, TMS) of compound (**6**)$_d$, (Figure 12.) shows the following features: two pairs of doublet (8H) at δ 8.25 – 7.75 ppm and δ 7.3 – 7.15 ppm. Triplet overlapping peaks (4H) at δ 4.25 – 4.13 ppm that could be assigned to OCH_2 protons. Multiplet (10H) overlapping peaks at δ 1.8 – 1.6 ppm due to –CH_2-CH_2- carbons. Triplet (6H) overlapping peaks at δ 1.00 – 0.93 ppm due to terminal CH_3 group.

The ^{1}HNMR (Acetone-d, TMS) of compound (**6**)$_g$, (Figure 13.) shows the following features: A pairs of doublet (8H) at δ 7.95 -7.7 ppm and δ 7.07 – 6.9 ppm. Triplet (2H) at δ 4.35 -4.20 ppm that could be assigned to OCH_2 protons. Multiplet (6H) at δ 1.05 – 1.39 ppm due to –CH_2-CH_2-CH_2. Triplet (3H) at δ 1.10 – 0.90 ppm due to terminal CH_3 group.

Table 3: Melting points and % yield of compounds $(6)_{a-j}$ and compounds $(11)_{a-e}$

Comp. name	Comp. No.	Yield %	m.p(°C)
3-(4-pentoxy phenyl)-5-(4′-methoxy phenyl)-1,2,4-oxadiazole	$(6)_a$	40	125-127
3-(4-pentoxy phenyl)-5-(4′-ethoxy phenyl)-1,2,4-oxadiazole	$(6)_b$	45	118-122
3-(4-pentoxy phenyl)-5-(4′-propoxy phenyl)-1,2,4-oxadiazole	$(6)_c$	50	127-133
3-(4-pentoxy phenyl)-5-(4′-butoxy phenyl)-1,2,4-oxadiazole	$(6)_d$	55	106-112
3-(4-pentoxy phenyl)-5-(4′-pentoxy phenyl)-1,2,4-oxadiazole	$(6)_e$	45	100-118
3-(4-pentoxy phenyl)-5-(4′-floro phenyl)-1,2,4-oxadiazole	$(6)_f$	44.2	130-135
3-(4-pentoxy phenyl)-5-(4′-chloro phenyl)-1,2,4-oxadiazole	$(6)_g$	52	136-141
3-(4-pentoxy phenyl)-5-(4′-bromo phenyl)-1,2,4-oxadiazole	$(6)_h$	60	148-154
3-(4-pentoxy phenyl)-5-(4′-iodo phenyl)-1,2,4-oxadiazole	$(6)_i$	43	160-162
3-(4-pentoxy phenyl)-5-(4′-nitro phenyl)-1,2,4-oxadiazole	$(6)_j$	60	146-156
3-(4-pentoxy benzoyloxyphenyl)-5-(4′- methoxy benzoyloxy phenyl)-1,2,4-oxadiazole	$(11)_a$	69	223-235
3-(4-pentoxy benzoyloxyphenyl)-5-(4′- ethoxy benzoyloxy phenyl)-1,2,4-oxadiazole	$(11)_b$	60	200-209
3-(4-pentoxy benzoyloxyphenyl)-5-(4′- propoxy benzoyloxy phenyl)-1,2,4-oxadiazole	$(11)_c$	54	197-207
3-(4-pentoxy benzoyloxyphenyl)-5-(4′- butoxy benzoyloxy phenyl)-1,2,4-oxadiazole	$(11)_d$	64	182-191
3-(4-pentoxy benzoyloxyphenyl)-5-(4′- pentoxy benzoyloxy phenyl)-1,2,4-oxadiazole	$(11)_e$	74	178-189

Table 4: characterization FTIR absorption bands of synthesizes compounds

Comp No.	*X- group*	*υ C-H Aro. cm^{-1}*	*υ C-H Aliph. cm^{-1}*	*υ C=N cm^{-1}*	*υ C=C cm^{-1}*	*υ C-O cm^{-1}*	*Others bands*
$(6)_a$	$-OCH_3$	3078.9	2904.5-2856.3	1610.2	1560.9	1240.5	
$(6)_b$	$-OC_2H_5$	3080.1	2981.7-2829.4	1606.6	1543.1	1263.3	
$(6)_c$	$-OC_3H_7$	3096.4	2935.5-2875.7	1604.7	1547.9	1250.0	
$(6)_d$	$-OC_4H_9$	3025.3	2953.8-2839.0	1608.0	1572.9	1257.5	
$(6)_e$	$-OC_5H_{11}$	3076.5	2974.0-2864.1	1602.7	1551.8	1257.5	
$(6)_f$	-F	3035.0	2943.7-2863.1	1600.8	1534.6	1228.6	(C-F) 1050.2
$(6)_g$	-Cl	3085.6	2959.4-2886.0	1605.7	1583.2	1238.2	(C-Cl) 1080
$(6)_h$	-Br	3077.1	2935.7-2848.7	1612.6	1581.5	1242.5	(C-Br) 578.9
$(6)_i$	-I	3025.6	2961.3-2839.0	1614.0	1591.2	1238.2	(C-I) 500.2
$(6)_j$	$-NO_2$	3021.5	2929.6-2854.5	1602.7	1575.7	1261.4	(NO_2) 1525.6 & 1346.2
Comp No.	*X- group*	*υ C-H Aro. cm^{-1}*	*υ C-H Aliph. cm^{-1}*	*υ C=O cm^{-1}*	*υ C=C cm^{-1}*	*υ C-O cm^{-1} Others bands*	
$(11)_a$	$-OCH_3$	3058.8	2934.6-2856.4	1739.7	1608.5	1259.5-1163.0	
$(11)_b$	$-OC_2H_5$	3080.2	2940.2- 2865.2	1740.2	1605.1	1255-1160.7	
$(11)_c$	$-OC_3H_7$	3056.9	2947.0-2852.5	1737.0	1600.8	1265.2-1159.1	
$(11)_d$	$-OC_4H_9$	3085.3	2925.8-2856.4	1743.0	1600.9	1267.1-1159.1	
$(11)_e$	$-OC_5H_{11}$	3070.4	2954.7-2874.1	1735.8	1596.9	1249.7-1157.2	

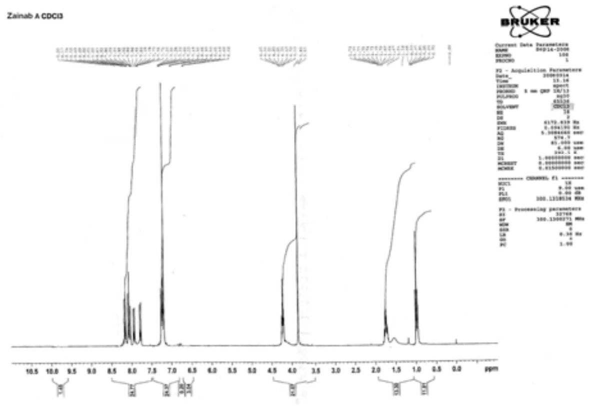

Figure 12: ^{1}HNMR spectrum of 3-(4-pentoxy-phenyl)-5-(4′-butoxy phenyl)-1,2,4 oxadiazole (6)$_d$

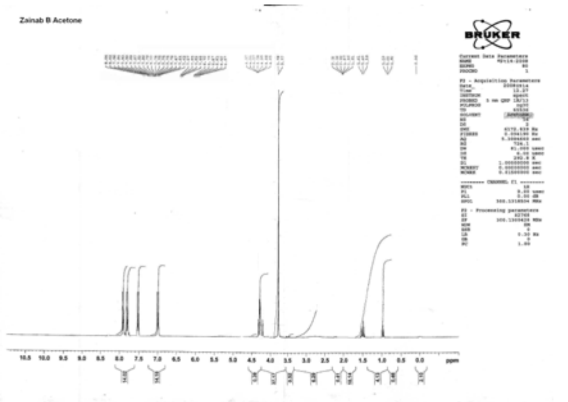

Figure 13: ^{1}HNMR spectrum of 3-(4-pentoxy phenyl)-5-(4′-butoxy phenyl)-1, 2, 4- oxadiazole (6)$_g$

The ^{1}HNMR (DMSO, TMS) of compound (**11**)$_d$, Figure 14. shows the following features: pair of doublets (8H) at δ 8.1 – 7.7 ppm, two doublets (8H) at δ 7.2 – 6.95 ppm. Triplet overlapping peaks (4H) at δ 4.00– 3.78 ppm that could be assigned to OCH_2 protons. Multiplet (10H) overlapping peaks at δ 1.6 – 1.4 ppm due to $–CH_2$-CH_2- carbons. Triplet (6H) overlapping peaks at δ 1.8 – 1.9 ppm due to terminal CH_3 group.

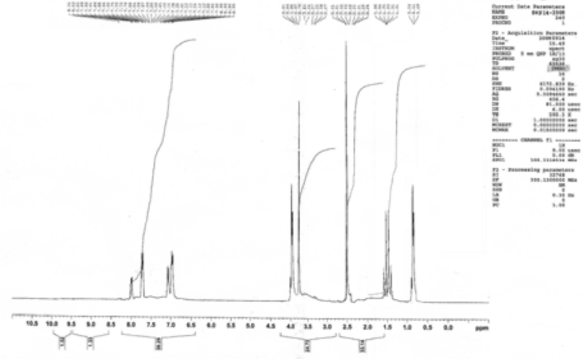

Figure 14: ^{1}HNMR spectrum of 3-(4-pentoxy-benzoyloxyphenyl) -1,2,4- oxadiazole(11)$_d$.

The ^{1}HNMR (DMSO, TMS) of compound (11)$_e$, Figure 15. shows the following features: A pairs of doublets (8H) at δ 7.94 -7.53 ppm and δ 7.14 – 7.08. Triplet (2H) at δ 4.2 -4.0 ppm that could be assigned to OCH_2 protons. Multiplet (12H) at δ 1.8 – 1.5 ppm due to –CH_2-CH_2-CH_2 of the two n-pentyl groups. Triplet at (6H) δ 1.0 – 0.9 ppm due to terminal CH_3 group.

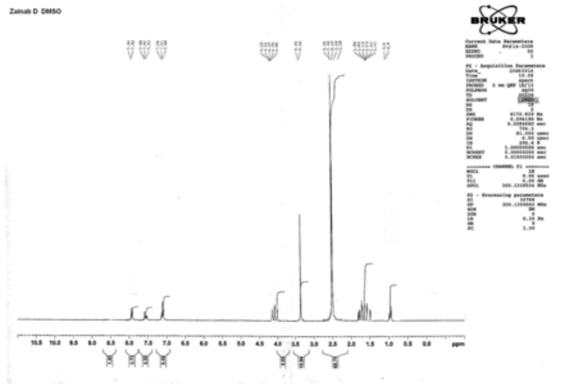

Figure 15: ^{1}HNMR spectrum of 3-(4-pentoxy-benzoyloxyphenyl)-5-(4′-pentoxy-benzoyloxyphenyl)-1,2,4- oxadiazole(11)$_e$

Conclusion

A variety of mesogenic 3,5-disubstituted 1,2,4- oxadiazoles have been synthesised. The results presented here show that this new class of liquid-crystalline compounds is very useful for investigating the correlation between the chemical structure of mesogens and their mesomorphic properties.

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