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Liquid Crystalline Behavior of Dimers Containing 1, 3, 4-Oxadiazole Unit

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Abstract

The synthesis and liquid crystalline properties of new series of 1,3,4-oxadiazole derivative are reported. (2-[(4-methoxy benzylidine amino)-5-(4-hydroxy-phenyl)]-1,3,4-oxadiazole) (II) was synthesized by condensation of (2-amino-5-(4-hydroxy phenyl)-1,3,4-oxadiazole) (I) with (anisaldehyde). A dimmer series with structural formula (III) were synthesis by dimmerization of compound (II) with appropriate (malonic acid, succinic acid, glutaric acid, adipic acid, and palmic acid). The liquid crystalline properties of dimmer series (III) was examined by hot-stage polarizing microscope and showed the presence of nematic mesophases.

Keyword: liquid crystal, 1,3,4-oxadiazole.

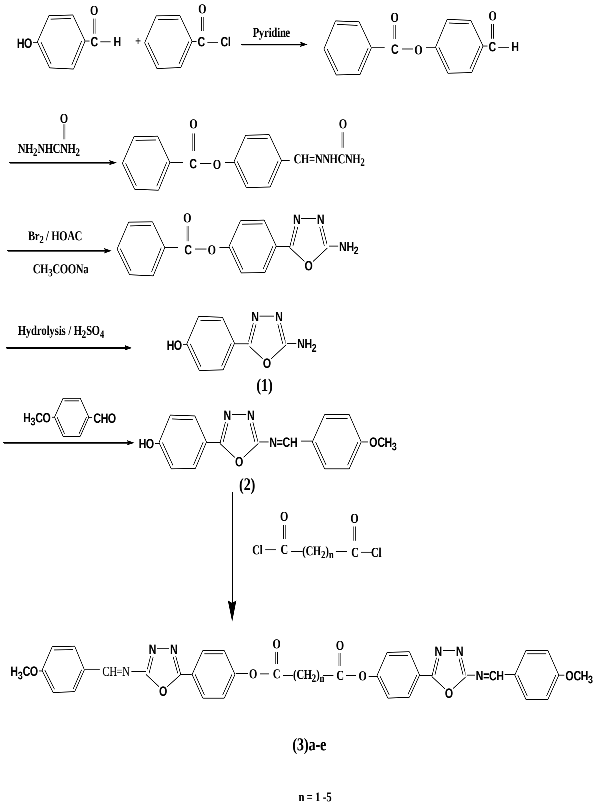
Introduction

Certain oxadiazoles compounds can reveal liquid crystalline features and in particular, as recently demonstrated can show the elusive biaxial nematic phase. Theoretically proposed in 1970 by Freiser[1], the biaxiality can be observed in the nematic phase of boomerang-shaped oxadiazoles[2,3]. In general, the oxadiazoles are interesting for applications to electroluminescent devices where they are the emissive materials[4]. The compounds are generally chemically stable, sometimes with good electron-transport properties. The study on these materials allows the conclusions that the presence of mesophases is affected by both electronic and steric factors within terminal substituents[5]. Smectic and nematic, enantiotropic and monotropic phases were observed with polarized light microscope.

Instrumental

Melting points were determined on a Gallen Kamp melting point apparatus and are uncorrected. The IR spectra were measured as potassium bromide pellets using a Shimadzu FTIR 8300 spectrophotometer. The transition temperatures for all compounds were determined by optical microscopy using Olympus BX40 Microscope equipped with a Link–AmTH600 hot stage and PR600 controlled. The H^1NMR spectra were recorded on a *Brüker ACF* 300 Spectrometer operating at 300 MH_Z in DMSO-d_6.

Preparation of compounds:



n	compound no.
1	a
2	b
3	c
4	d
5	e

Scheme (I)

1-2-amino-5-(4-hydroxy phenyl)-1,3,4-oxadiazole (I): was prepared according to literature[6]. M.p. 225-227°C, yield (76%); IR (KBr) (ν, cm^{-1}), 3500(OH), 3400-3200 (NH_2), 3100 (C-H aromatic), 1280-1240 (C-O), 1640 (C=N), 850 (*p*- disubstituted benzene ring).

2- (2-[(4-methoxy benzylidine amino)-5-(4-hydroxy-phenyl)]-1,3,4-oxadiazole) (II)[7]*:*

A mixture of the compound (I)(1gm, 0.01 mole), and (5ml) of (anisaldehyde) was heated for 4 hours on a oil bath at 200°C. Then the mixture was poured onto ice. A pale yellow precipitated was formed, which was filtered and dried. Yield 40%; mp. 175-176˚C; IR (KBr) (ν, cm^{-1}), 3400-3225 (OH), 3095 (C-H aromatic), 1680 (C=N), 1510 (C''''''C aromatic), 1170-1120 (C-O), 844 (*p*- disubstituted benzene ring).

3- di-[2-(4'-methoxy benzylidine amino)-5-(4''-oxophenyl-1,3,4-oxadiazole)carboxylate).

These compounds were prepared by adding drop wise the appropriate acid chloride (0.01 mole) to (0.02 mole) of compound (II) that was dissolve in (5 ml) dry pyridine. The mixture was stirred for three hours at room temperature, and then it was poured into cold water. The precipitate filtered, washed with 0.1 M HCl solution and saturated solution of sodium bicarbonate then by distilled water. Table (1) shows the melting points and % yield of the synthesized compounds.

Table (1)
Melting points and % yield of compounds (3)a-e.

n	*Comp.No.*	*Yield %*	*m.p(°C)*
1	$(3)_a$	88%	215-216°C
2	$(3)_b$	91%	202-204°C
3	$(3)_c$	65%	240-241°C
4	$(3)_d$	72%	165-166°C
5	$(3)_e$	76%	224-226°C

Results and Discussion

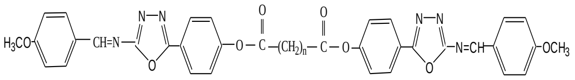
2-amino -5- (4-hydroxy phenyl) -1,3,4-oxadiazole (1): was prepared according to method described by Al-duijali et.al.[6] through the oxidative cyclization of semicarbazone with bromine, in the presence of anhydrous sodium acetate in glacial acetic acid, as shown in the scheme of preparation the aldehydes first converted to ester, this step is important to avoid the oxidation of hydroxyl group of 4-hydroxy Benzaldehyde to keto form.

(2-[(4-methoxy benzylidine amino)-5-(4-hydroxy phenyl)]-1,3,4-oxadiazole) (2): This compound was prepared from the reaction of compound (1) with (anisaldehyde).

Dimmer 3(a-e).

This new series of dimmer were prepared by dimmerization of compound (II) with appropriate diacid chlorides in dry pyridine. The appearance of absorption bands which are due to (C=O) at 1735 cm^{-1} and (C=N) at (1602-1610) cm^{-1} is a good evidence for the formation of the derivatives 3 (a-e). The FTIR spectra also show band at 3435-3400 cm^{-1} could be assign to the stretching of the O-H of enole form. Table (2) shows the FTIR bands of the synthesizes compounds.

Table (2)
Characteristic FTIR absorption bands of synthesizes compounds.



comp. No.	*(6)a*	*(6)b*	*(6)c*	*(6)d*	*(6)e*
n	**1**	**2**	**3**	**4**	**5**
υ C-H aro. cm^{-1}	**3078.9**	**3080.1**	**3096.4**	**3025.3**	**3076.5**
υ C-H alpht cm^{-1}	**2904.5-2856.3**	**2981.7-2829.4**	**2935.5-2875.7**	**2953.8-2839.0**	**2974.0-2864.1**
υ C=N cm^{-1}	**1610.2**	**1606.6**	**1604.7**	**1608.0**	**1602.7**
υ C=C cm^{-1}	**1560.9**	**1543.1**	**1547.9**	**1572.9**	**1551.8**
υ C=O cm^{-1}	**1697.2**	**1735.1**	**1720.1**	**1697.2**	**1688.9**
υ C-O cm^{-1}	**1240.5**	**1263.3**	**1250.0**	**1257.5**	**1257.5**
γ C-H out of plane para-subs. cm^{-1}	**821.6**	**827.4**	**823.5**	**846.7**	**840.9**

Table (3) summarizes the mesomorphic behavior of the series **(3)a-e** with various number of (CH_2) group. The ^{1}HNMR spectrum of compound (3)a show the following: (DMSO-d6, TMS, 300 MHz); δ ppm =8.2-7.8 (d, 4H, arom. H) for the ring attach to oxadiazoles ring; 7.47-6.58 (d, 4H, arom. H);

8.46 (s, 2 H, imine); 3.82 (s, 6H, OCH$_3$); 2.08 (s, 2H, CH$_2$).

The ^{1}HNMR spectrum of compound (3)b show the following: (DMSO-d6, TMS, 300 MHz); δ ppm =8.82-7.76 (d, 4H, arom. H); 7.64-6.76 (d, 4H, arom. H); 8.84 (s, 2 H, imine); 3.64 (s, 6H, OCH$_3$); 3.43 (t, 4H, CH$_2$-CH$_2$).

The ^{1}HNMR spectrum of compound (3)c show the following: (DMSO-d6, TMS, 300 MHz); δ ppm =8.47-7.70 (d, 4H, arom. H); 7.67-6.87 (d, 4H, arom. H); 8.51 (s, 2 H, imine); 3.86 (s, 6H, OCH$_3$); 3.72 (p, 2H, CH$_2$-$\underline{CH_2}$-CH$_2$); 2.12 (t, 2H, $\underline{CH_2}$-CH$_2$-CH$_2$); 1.23 (t, 2H, CH$_2$-CH$_2$-$\underline{CH_2}$)

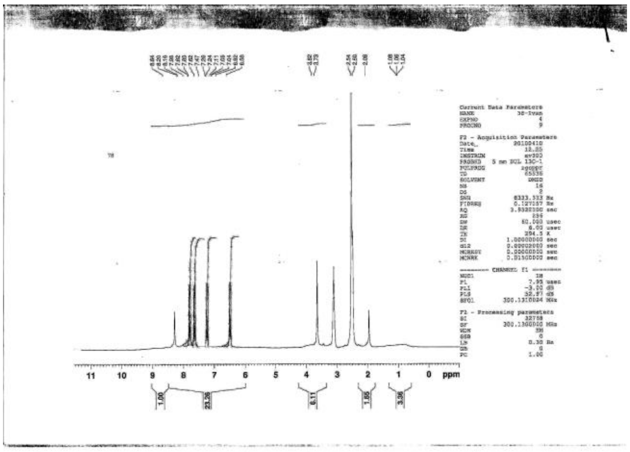


Fig. (1) ^{1}HNMR spectrum of compound (3)a.

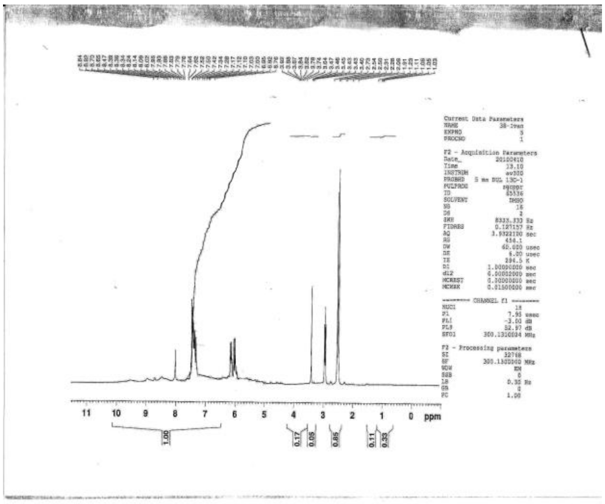


Fig. (2) ^{1}HNMR spectrum of compound (3)b.

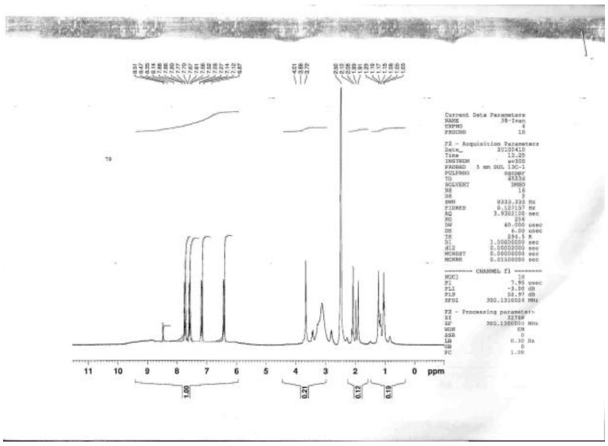


Fig. (3) ^{1}HNMR spectrum of compound (3)c.

Table (3)
Summarizes the mesomorphic behavior of the series (3)a-e with various number of (CH$_2$) group.

Comp. No.	*N*	*Transition*	*T °C*	*T °C Hot stage*
(3)$_a$	**1**	C → I	215°C	215-217°C
(3)$_b$	**2**	C → I	202°C	202-204°C
(3)$_c$	**3**	C → N C → I	240°C	240-248°C
(3)$_d$	**4**	C → N C → I	165°C	164-172°C
(3)$_e$	**5**	C → N C → I	224°C	222-231°C

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

As can be observed in Table (3), the melting point decreases slightly with increase in the chain length. Microscopic observations of compounds of **(3)$_{a-e}$** at liquid crystalline transition temperature displayed a nematic mesophase of typical nematic droplets are observed on cooling from the isotropic liquid Figs. (1-3),

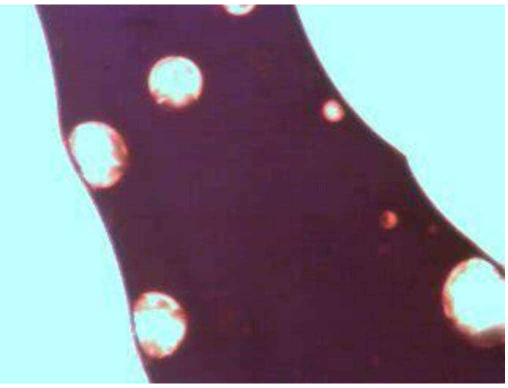


Fig. (1) Nematic texture of model compound (3)$_a$.

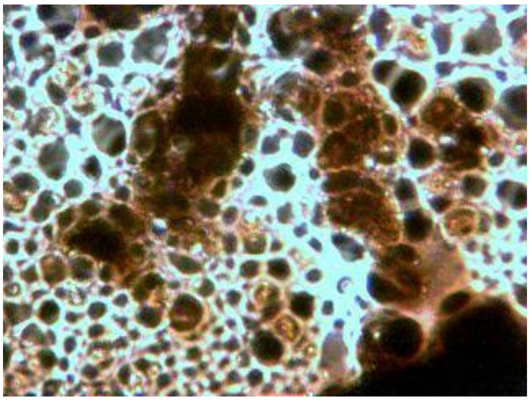


Fig. (2) Nematic texture of model compound (3)$_b$.

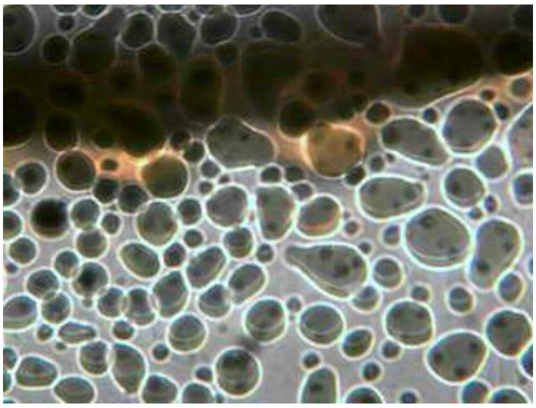


Fig. (3) Nematic texture of model compound (3)$_c$.

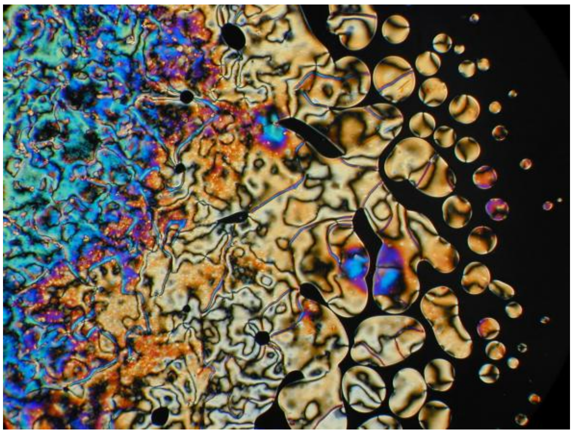


Fig. (4) Nematic texture of model compound (3)$_d$.

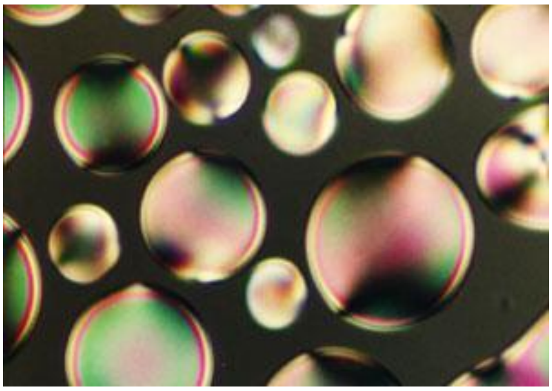


Fig. (5) Nematic texture of model compound (3)$_e$.

Conclusion

This new class of liquid-crystalline compounds is a very interesting object for a study of correlation between the structure of compounds and their mesomorphic properties

i) Lowering the isotropic transition temperature slightly.
ii) Lowering liquid-crystal transition temperature considerably.
iii) Change the mesophases type.

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الخلاصة

لقد تم تحضير والتعرف على خواص البلورات السائلة لسلسلة جديدة من مشتقات 1و3و4-اوكسادايازول. ان (2-[(4-ميثوكسي امينوبنزلدين)- 5-(4-هايدروكسي فنيل)-1و3و4-اوكسادايزول) (II) قد حضر بواسطة تكثيف ((2-امينو) - 5-(4-هايدروكسي فنيل)-1و3و4-اوكسادايزول) (I) مع (الانيسالديهايد) . ان سلسلة البوليمر الثنائي مع الصيغه الجزيئيه (III) تم تحضيره من خلال البلمرة الثنائية للمركب (II) مع مجموع ة من (كلوريدات الحوامض الكاربوكسيلية الثنائية) .ومن تم اثبات خواص البلورات السائلة باستخدام مجهر مستقطب مزود بمسخن حراري.