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# Azomesogens with tetra substituted benzene

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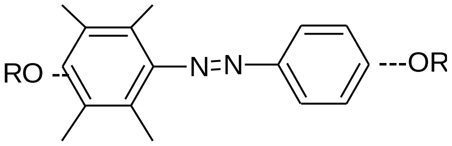
## Abstract.

**In the present study , new series compounds : ( ٤-n- Alkoxy -٢،٣،٥،٦ –tetra methyl phenyl – ٤-n-alkoxy azo benzene .) homologues have been synthesized and characterized by IR ,HNMR , and elemental analysis , the mesomorphic character of the character of the compounds was studied by using differential scanning calorimeter (DSC) and polarizing microscope equipped with heating and cooling stage . To study the effect of the lateral groups on the thermal stabilities of the mesophase of the series, and the acting of broadening groups.**



**R = Cn H٢n +١ n = ١, ٢،٣،٤،٥،٦،٧،٨**

## ١. Introduction

Until ١٩٨٣ it was generally accepted that lateral substituents diminish the mesogenic property of a compound, the extent of the effect depending on their size *P.G. de genes* / ١ /, *J. Godzwon et al* /٢/. As found by Weissflog and Demus /٣, ٤/, surprisingly, compounds with large flexible lateral substituents exhibit liquid crystalline phases. They also reported Weissflog and Demus/٥/ compound containing two long chain lateral substituents that are nematic. Cox *et al* /٦/ synthesized nematogens in which lateral phenyl group is attached without a spacer. Gallardo and Muller /٧/, Weissflog and Demus /٨/ and Weissflog *et al* /٩, ١٠/ also reported mesogens with Lateral aromatic substituents. Subsequently numbers of homologous series with trisubstituted benzene nucleus have appeared in the literature

(Baumeister *et al* /١١/; Diele *et al* /١٢/; Berdague *et al* /١٣/ ; Weissflog *et al* /١٤/ ; Weissflog and Jacobi /١٥/ ; Perez *et al* /١٦/ ). Vora *et al* /١٧/ reported four mesogenic homologous series containing three rings in the main core and substituted by a lateral aromatic branch or hydroxy group on the central benzene nucleus. The mesogenic homologous series with lateral hydroxyl group exhibited nematic mesomorphism whereas homologous series with lateral aromatic branch exhibited smectogenic tendencies. also banana-shaped monomers compounds exhibited nematic mesophase with lateral florid group Md Lutfor Rahman *et al* /١٨/. In the present work, we have introduced lateral methyl group on one of the benzene ring in order to study the effect of such groups on the mesomorphic properties and transition temperatures as this group will lower the transition temperatures. Further, the effect of four methyl lateral group has not been studied and this prompted us to carry out the present work.

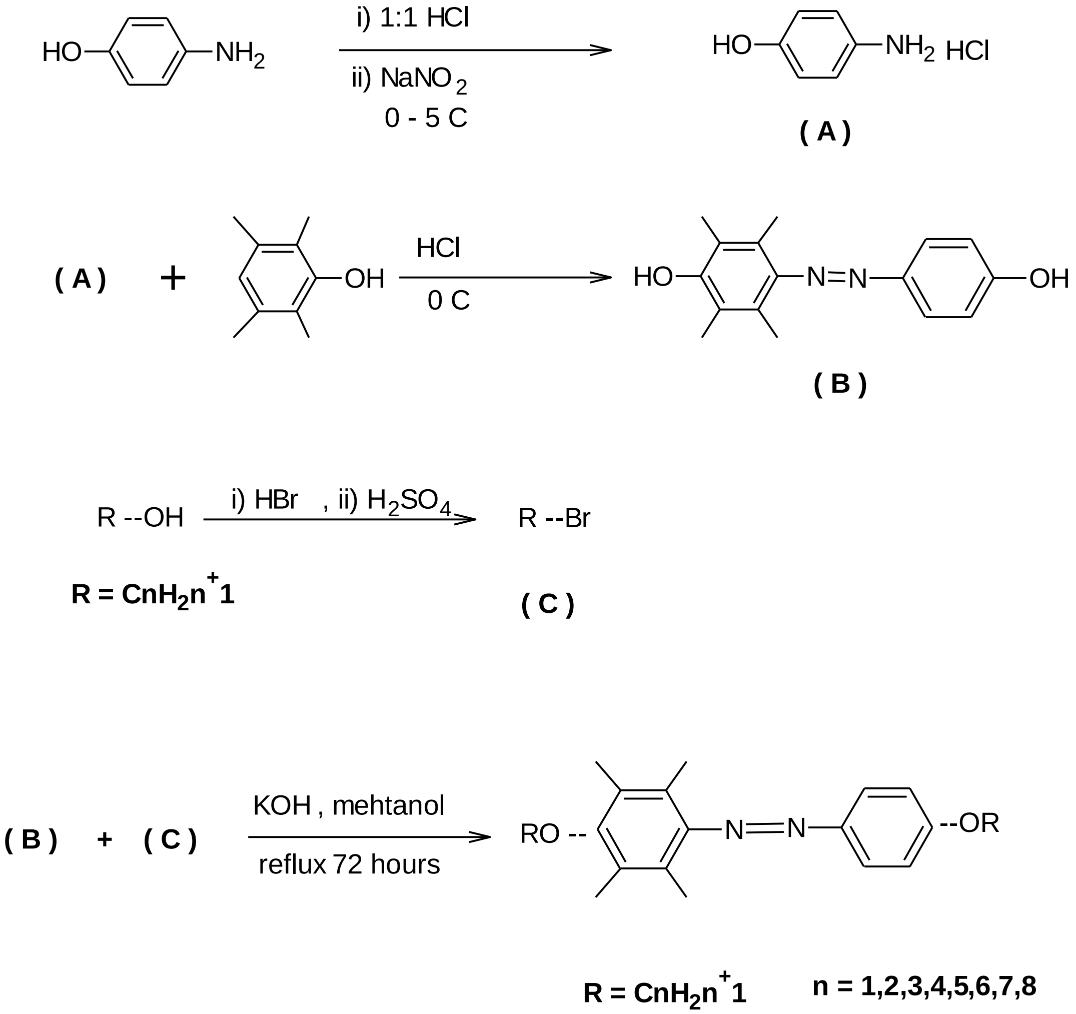
## ٢. Experimental

### ٢,١ *Characterization*

Microanalysis of the compounds were performed on a Perkin – Elmer ٢٤٠ B elemental Analysis (C,H,N), and IR spectra were recorded on PU ٩٧١٢ infrared spectrophotometer ( Phillips ) using KBr pellets, H NMR spectra were recorded on Bruker WH ٩٠ DS spectrometer equipped with an ASPECT٢٠٠٠ , ٣٢ computer , operating at ٢٢-٦٣ MHz using TMS as a standard. The calorimetric studies were carried out on ٩١٠ Differential Scanning Calorimeter (DSC)١٠٩٠ thermal analyzer (Phillips ) apparatus by adopting a scanning rate of ١٠°C/min. Liquid crystalline properties were investigated on a Olympus microscope provided with a heating & cooling stage. Which good agreement with DSC data.

### ٢,٢ *Synthesis*

All chemicals were from BDH, Riedel – dean AG sellze – Hanover, Fluka–Garantie , Aldrich , Hopkin and Willams and used as received . All the solvents were dried and distilled prior to use.The compounds of the new series were prepared following the pathway shown in scheme١.



**SYNTHETIC ROUT TO THE SERIES**

**Scheme ١**

٢,٢ a : *٤ – hydroxyl dizonium benzene* ( A) , ٤ –hydroxy -٢،٣،٥،٦ – tetra methyl azo phenol ( B ) and n –alkyl bromide ( C ) . These compounds were synthesized according to description in Vogel ١٩٧٣ / ١٩ /.

٢,٢.b : *٤ – n – alkyl oxy – ٢،٣،٥،٦ – tetra methyl phenyl - ٤-n- alkyloxy azo benzene* this synthesis is described elsewhere in Wilfrid G *et al*

/ ٢٠ /.

Finally all products were crystallized from alcohol till constant transition temperatures were obtained .The elemental analysis (table ١) of all compounds were found to be satisfactory.

IR ( KBr ) spectra : ( Vmax , Cm ) : ٣٠٨٠ – ٣٠٠٠ ( aromatic C- H ) , ٣٠٠٠ – ٢٨٠٠ ( aliphatic C – H ) , ١٥٩٠ , ١٥٧٥ ( -N=N- ) , ١٢٤٥ , ١٢٤٠ ( aromatic C – O – C ) .

HNMR spectra ( solvent $CDCl_{٣}$ , ٦٠ MHz ) : O ٠,٩ ( t , ٣H , -$CH_{٣}$ ) , ١،٤ – ١،٧ ( m ٤H , ٢x – $CH_{٢}$- ) ٢،١ -٢،٣ ( s , ٣H – Ph -$CH_{٣}$ ) , ٣،٨ -٤ -١ ( t , ٢H , - $OCH_{٢}$ -) , ٧،١ -٨ ( m ,٤h at C-٣ ,C-٥ , C-٢ and

C-٦ ) .

Table ١. Elemental data of the sires

| Compound , no. | R=-Cn H٢n+١ N٢ O٢ | | Required ( % ) | | | Found ( % ) | | |
|---|---|---|---|---|---|---|---|---|
| | n = | formula | N | C | H | C | H | N |
| ١ | ١ | $C_{١٨}H_{٢٢}N_{٢}O_{٢}$ | ٧٢,٤٨ | ٧,٣٨ | ٩,٣٩ | ٧١,٦٠ | ٧,٤٧ | ٨,٦٥ |
| ٢ | ٢ | $C_{٢٠}H_{٢٦}N_{٢}O_{٢}$ | ٧٣,٦١ | ٧.٩٧ | ٨,٥٨ | ٧٣,٧٠ | ٧,٨٨ | ٩,٠٣ |
| ٣ | ٣ | $C_{٢٢}H_{٣٠}N_{٢}O_{٢}$ | ٧٤,٥٧٢ | ٨,٤٧ | ٧,٩٠ | ٧٥..٢٦ | ٧,٧٤ | ٨,٨٥ |
| ٤ | ٤ | $C_{٢٤}H_{٣٤}N_{٢}O_{٢}$ | ٧٥,٣٩ | ٨,٩٠ | ٧,٣٢ | ٧٧,٢٨ | ٩,٥٧ | ٧,٢ |
| ٥ | ٥ | $C_{٢٦}H_{٣٨}N_{٢}O_{٢}$ | ٧٦,٠٩٧ | ٩,٢٦ | ٦,٨٢ | ٧٦,٠٤ | ٩,٤٦ | ٦,٨٥ |
| ٦ | ٦ | $C_{٢٨}H_{٤٢}N_{٢}O_{٢}$ | ٧٦,٧١٢ | ٩,٥٨٩ | ٦,٣٩ | ٧٧,٤٥ | ٩,٥٩ | ٦,٠٠ |
| ٧ | ٧ | $C_{٣٠}H_{٤٦}N_{٢}O_{٢}$ | ٧٧,٢٥ | ٩,٨٧ | ٦,٠٠ | ٧٧,٥٥ | ٩,٩٤ | ٦,٣٤ |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ٨ | ٨ | $C_{٣٢}H_{٥٠}N_{٢}O_{٢}$ | ٧٧,٧٣ | ١٠.١٢ | ٥,٦٦ | ٧٨,٩٧ | ١٠,٢٩ | ٦,٧٤ |

## ٣. Results and discussion

The transition temperatures for compounds of the series are recorded in (table ٢), which have good agreement with DSC data. Also it is a valuable method for the detection of phase transitions. Eight homologues have been synthesized and five of these homologues of the series (n = ٤،٥،٦،٧،٨ ) *٤-n- alkyloxy – ٢،٣،٥،٦, tetra methyl – ٤ – n – alkyloxy azo benzene* .Exhibit monotropic smectic and nematic phases . Schlieren texture, as typical for nematic phases and the smectic texture look like Sm E or Sm I phase texture (figure ٢). DSC graph (figure ١) shows the transition points of the two monotropic phases (isotropic to nematic and nematic to smectic phases) in the exothermic process.

In our case the measurements were taken in the cooling process after the samples were heated more than the melting point in ١٠ C, figure ١ show the transition temperature in the heating and cooling process for the homologues *(٤- n – octyloxy – ٢،٣،٥،٦, tetra methyl - ٤ – octyloxy azo benzene).*

It is clear from the plot of the transition temperature against the number of carbon atoms in alkyloxy chain (figure ٣).

That the nematic – isotropic transition temperature Exhibit the usual alternation associated with homologous series of mesomorphic ethers Containing alkyl chain. Hence these transitions points on two falling curves , the upper One determined by those ethers containing an even number of carbon atoms , and the lower by those with an odd number of carbons in the alkyloxy chain. As a result of this alternation, the highest nematic – isotropic transition temperatures found for butyl ether ٨٥ C. the transition temperature between the nematic and the smectic phase don't show clear alternation with the increasing of the alkyloxy chain.

Table ٢ the transition temperature(C) of the present series

|  |  | Transition temperatures (C) |  |  |  |
|---|---|---|---|---|---|
| Compound No. | R= $C_nN_{٢n+١}$ n = | Cr | Sm | N | I |
| ١ | ١ | • ١٢٩ | - | - |  |
| ٢ | ٢ | • ١٢٦ | - | - |  |
| ٣ | ٣ | • ١٠٣ | - | - |  |
| ٤ | ٤ | • ٨٩ | • (٨٣) | • (٨٥) |  |
| ٥ | ٥ | • ٨٧ | • (٥٩) | • (٦٢) |  |
| ٦ | ٦ | • ٨٠ | • (٤٨) | • (٦٣) |  |
| ٧ | ٧ | • ٦٩ | • (٤٧) | • (٥٤) |  |
| ٨ | ٨ | • ٦٥ | • (٤٥) | • (٦١) |  |

Figure ١

DSC graph transition points of

٤- n – octyloxy – ٢،٣،٥،٦, tetra methyl -٤ – octyloxy azo benzene

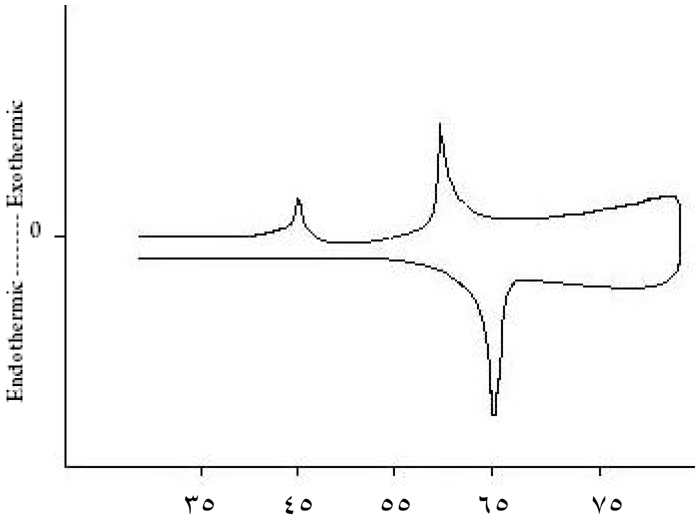
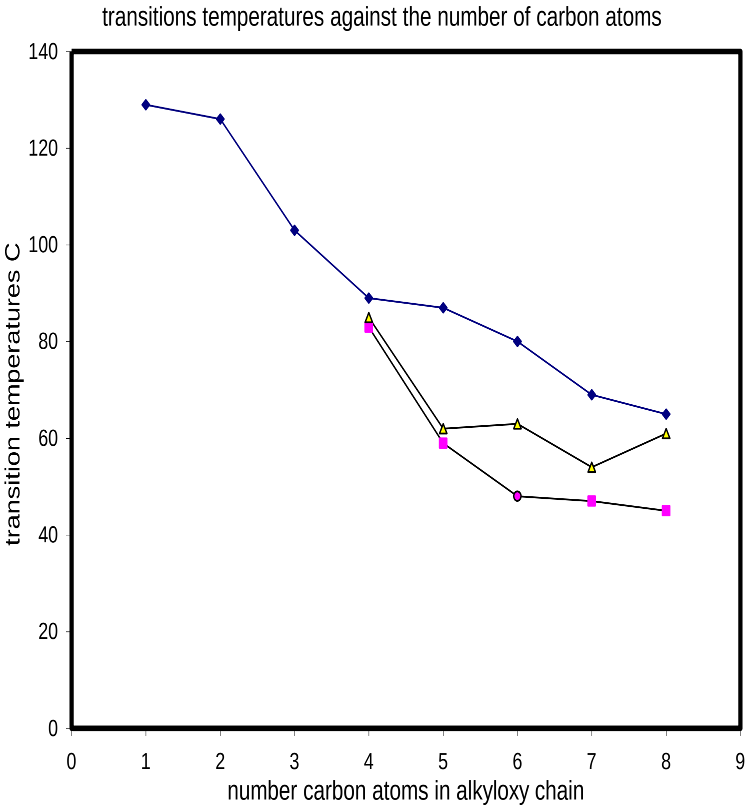


Figure٢
The smectic & nematic phases

A) Smectic phase B) Nematic phase

Figure ٣



## ٤. Conclusions

New mesogenic homologous series with four lateral methyl groups on one of the central benzene ring were synthesized. The four methyl lateral groups are acting as broadening groups on the molecules of the series compounds, these groups increase the diameter of the molecule and change the ratio between the length and diameter of the molecule ( L / D ) , where is L the length and D is the diameter of the molecule. According to this reason the homologous compounds with alkyloxy terminal groups of (n= ١, ٢, ٣) have no mesophase, on second hand affected the lateral groups on the thermal stabilities of the mesophase. The homologous compounds with terminal alkyloxy groups ( n = ٤،٥،٦،٧،٨ ) show for fist time high orientation order smectogenic to nematogenic transition , adversely affect the four lateral groups on the mesophase thermal stabilities. However, the increasing of the aliphatic terminal groups (alkyloxy) length decrease the transition temperature points of the mesophase and the melting points.

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# تحضير سلسلة جديدة من البلورات السائلة - آزوميزوجينز رباعية التعويض عند حلقة البنزين .

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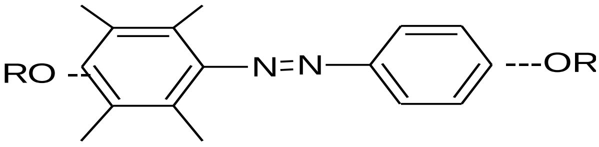
## خلاصة البحث

**في الدراسه الحالية ،تم تحضير سلسلة جديدة لمركبات بلورية سائلة**
**٤-n-Alkoxy-٢،٣،٥،٦-tetra methyl phenyl-٤-n-alkoxy azo ( benzene )**



**R = Cn H٢n +١ n = ١, ٢،٣،٤،٥،٦،٧،٨**

**ودرست خواصها التكوينية باستخدام التقنيات التاليه IR , HNMR , ( CHN ) .**
**كما تم تحديد ودراسة الحالات البلورية السائلة باستخدام مجهر الضوء المستقطب**
**( polarizing microscope ) مع منصة تسخين وتبريد و طريقة المسح التفاضلي المسعري (DSC) . وكان الهدف من هذة الدراسة هو لبيان مدى تاثير المجاميع الموسعة**

(مجاميع المثيل الموجودة على احدى حلقات البنزين ) على استقرار الحالة البلورية السائلة حراريا للسلسلة . وماهي الاطوار البلورية السائلة التي يمكن الحصول عليها .