

Preparation of azo compounds as liquid crystals

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Abstract

A new homologous series of symmetric dimers : α,β - Bis(4-n-alkoxy-2,3,5,6-methyl-4-oxy-Azo-benzene)ethane (n=1-7).have been synthesized and characterized by , IR, $^1\text{H-NMR}$ and CHN analysis. Their liquid crystalline properties have been determined by polarizing optical microscopy (pom).All the members except the member (n=1) show mesomorphic properties. The members (n=2,3) show enantiotropic pure nematic phase while the members (n=4-7) show entiotropic smectic C phase in addition to enantiotropic nematic phase .

Introduction

In liquid crystalline materials, mesomorphic properties appear in different temperature intervals. There are many types of mesophases which may be identified by their individual texture when investigated by polarized optical microscopy (pom)or by differential scanning calorimetry (DSC) , which clearly evidence the transition temperatures and the values of enthalpy transitions [1].The liquid crystalline state is characterized by the orientational ordering of its constituent molecules and transition between different mesophases are accompanied by change in the local molecular order . this transition are usually marked by change in various anisotropic properties , but depending on the order of transition they may also , accompanied by changes in scalar quantities such as enthalpy content or density [2-8] .The initial interest in liquid crystal dimers arose from their potential use as model compounds with which to understand the more complex polymeric systems . It quickly became apparent ,however, that the dimers themselves were of significant interest in their own right as they exhibited quite different behavior to conventional low molar mass liquid crystal [8,9] . The liquid crystal dimer consists of mesogenic units separated by flexible spacer normally alkyl chain [10].The azobenzene class of chromophores is characterized by the azo linkage (-N=N-) that bridge to phenyl rings. This extended aromatis structure give rise to azobenzenes intense optical absorption and related optical properties [11] .In this study we combine 4-alkyloxy-2,3,5,6-tetramethyl azobenzene units through flexible spacer to produce a calamitic symmetric liquid crystalline dimers with aim to study the liquid crystalline properties .

Experimental

1) Materials all unsynthesized compounds were commercial products of analar grade and were used without further purification .

2) Instrumentation

Analytical data were performed on micro analytical unit Euro vector S.P.A.E.A 300-CHN Elemental Analyzes . FT-IR Spectro were recorded on schimadzu FT-IR 84005 fourier transform infrared spectrophotometer (KBr disc) $^1\text{HNMR}$ spectra were recorded in CDCl_3 on NMR-Bruker spectrometer,400 MHz , with CDCl_3 at department of chemistry kashan

university Iran . The phase transition temperature for investigated compounds were determined using optical microscopy equipped with amettler hot stage .

3) synthesis (schem 1)

a) P-acetamido phenol 1

In abeaker containing 500ml of distilled water ,18.3 ml of concentrated hydrochloric acid and 23.48g of p-aminophenol were introduced . The mixture was stirred until the amine completely passes into solution .the solution was colored , So 3-4g of decolourising carbon was added and warmed to about 50C° with stirring for 5 minutes, filtered at pump to the resulting solution 25.6ml of acetic anhydride with three drops of sulphuric acid were added and stirred ,and then immediatly was poured in a solution of 33g of crystallized sodium acetate in 100ml of water . The solution was stirred vigorously and cooled in ice .The aceamido phenol was filtered with suction washed with a little distilled water ,and dried upon filter paper in air,m.p.168-169C° FT-IR(KBr pellet,cm⁻¹): 3325cm⁻¹(OH,phenol),3161 cm⁻¹(NH,amid),3043 cm⁻¹(C=C,aromatic) , 3109 cm⁻¹(C=C,aliphatic), 1642cm⁻¹(C=O,amide),1610cm⁻¹(C=C,aromatic).

b)1,2-Dibromo ethane

In a 500ml three necked flask fitted with reflux condenser and dropping funnel , 50ml of 48 % hydrobromic acid was placed .The flask was cooled in an ice bath. 35ml of concentrated sulphuric acid was added with stirring using magnetic stirrer.To the resulting ice-cold solution 9ml 0.165mol , of 1,2-dihydroxy ethane (glycol) was added . The reaction mixture was left to stand for 24 hours then heated for more than 5 hours on steam bath. The reaction mixture was separated into two layers, The lower layer was separated ,washed successively with water ,10 per cent. sodium carbonate solution and water and then dried with anhydrous magnesium sulphate . 4ml (0.05mol) it used without further purification.

c) 4,4'- Diacetamido - α - β -diphenoxy ethane 2

In an Erlenmeyer flask 250ml equipped with a dropping funnel and a water condenser, (15.1g,0.1mol) of p-acetamido phenol was dissolved into 75ml of hot ethanol with magnetic stirring .After cooling (7g,0.125mol)of KOH dissolved in 5ml of water was added slowly through the dropping funnel .then using the same dropping funnel 1,2-dibromoethane(4.26ml,0.05mol) dissolved in 25ml of ethanol, was added dropwise to the mixture .The mixture was refluxed for 4 hours after the end of the addition and then 25ml of distilled water was poured into it. After cooling of mixture , the solid obtained was filtered off , washed twice or three times with water until the filtrate was neutral and recrystallized from ethanol. ,m.p269-270C°FT-IR (KBr pellet,cm⁻¹), 3313 cm⁻¹ (C=O, amide),3134 cm⁻¹ (CH, aromatic), 2943 cm⁻¹ (CH, aliphatic),1661 cm⁻¹(C=O, amide), 1599cm⁻¹ (C=C,aromatic) .

d) 4,4'- Diamino - α - β -diphenoxy ethane 3

In around bottomed flask equipped with adropping funnel and a water condenser ,a mixture of4,4'- Diacetamido - α - β -diphenoxy ethane(8.2g,0.025mol) and ethanol (25ml) was refluxed. Then through the dropping funnel, 20N potassium hydroxide (12.5ml)was added slowly. After the end of the addition , the reaction mixture was refluxed for 70 hours . then after cooling 25ml of water was added into it. The solid was filtered off washed with water until the filtrate was neutral and recrystallized from ethanol. ,m.p179-180C°FT-IR (KBr pellet,cm⁻¹), 3325 cm⁻¹,3404 cm⁻¹ (NH, amine),3088 cm⁻¹ (CH, aromatic), 2945 cm⁻¹

(\square CH, aliphatic), 1627 cm^{-1} (\square NH, amide), 1510 cm^{-1} (\square C=C, aromatic), 1222 cm^{-1} (\square C-O-C, ether).

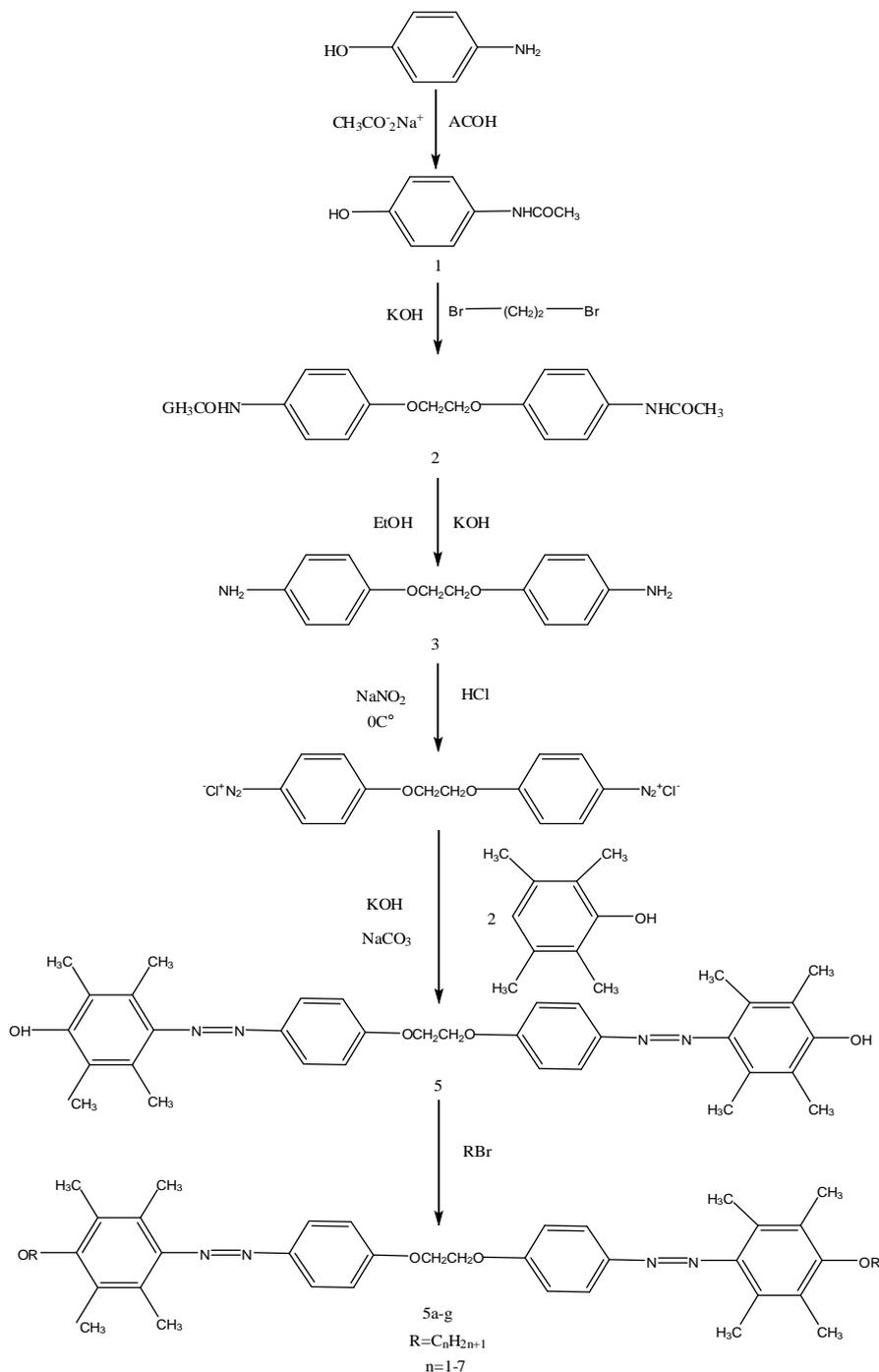
e) α,β - Bis(4- hydroxy-2,3,5,6-tetra methyl-4-oxy-Azo benzene)ethane 4
 In mixture of (0.5g,0.002mol) of the diamino 3 and 2.5ml HCl , 2.5ml water were cooled to 0-5C° with ice-salt bath to which (0.29g,0.004ml) of NaNO₂ dissolved in water 3ml was added dropwise under stirring .After the addition was completed the mixture was stirred for 30 minutes at 0C°.The diazonium salt was slowly added over a solution containing (0.6g.o.004mol) of 2,3,5,6-tetramethyl phenol, NaOH (0.16g,0.004mol) in 14ml water and (1g) of sodium carbonate at 5C°. After 3 hours, the brown precipitate was filtered off and washed several times with water m.p (247C°) FT-IR (KBr pellet, cm^{-1}) 3321 cm^{-1} (\square OH,phenol), 3022 cm^{-1} (\square CH,aromatic) ,2928 cm^{-1} (\square CH,aliphatic),1599 cm^{-1} (\square C=C,aromatic) ,1556 cm^{-1} (\square N=N, amine).

f) n-alkyl bromide

In a round bottomed flask equipped with a separatory funnel and a condenser set downward for distillation ,(71ml) of 48 % hydrobromic acid and (16.5ml) of concentrated sulphuric acid dropwise was added with stirring .After cooling (0.5mol)of the appropriate alcohol was added in portions ,The end of the condenser was connected to an adapter dipping into water contained in a 250ml flask, The later was surrounded by ice. (2.5ml) of concentrated sulphuric acid was introduced gradually through the separatory funnel and the mixture was distilled slowly until no more oily drops pass over . The organic layer was separated , washed successively with water , 10 % sodium carbonate solution and then with water , dried over anhydrous magnesium sulphate .it is used without further purification .

g) α,β - Bis(4-n-alkoxy-2,3,5,6-tetra methyl-4-oxy-Azo benzene)ethane 5

The compound 4 (3g,0.0123mol) was dissolved in a solution containing (1.85g,0.003 mol) KOH and 2ml water and 8ml ethanol ,A trace of potassium iodide was added and the solution was heated and stirred while 0.0136 mol of the appropriate n-bromoalkane was added slowly. The mixture was refluxed for 15 hour . The precipitate was filtered off ,washed several times with water ,until the filtrate is neutral . then recrystallized from ethanol .For the characterization of these compounds see discussion .



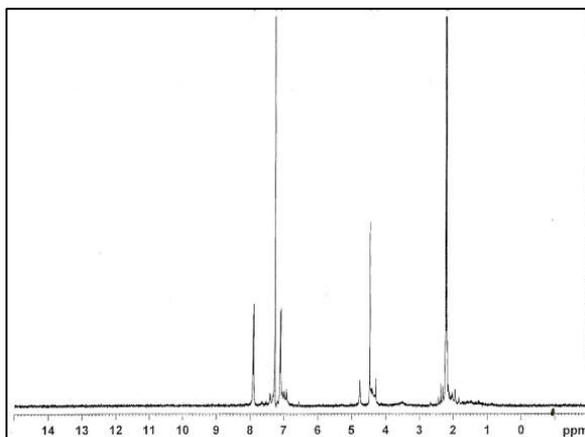
Scheme (1) Synthesis of the liquid crystals

Results and Discussion

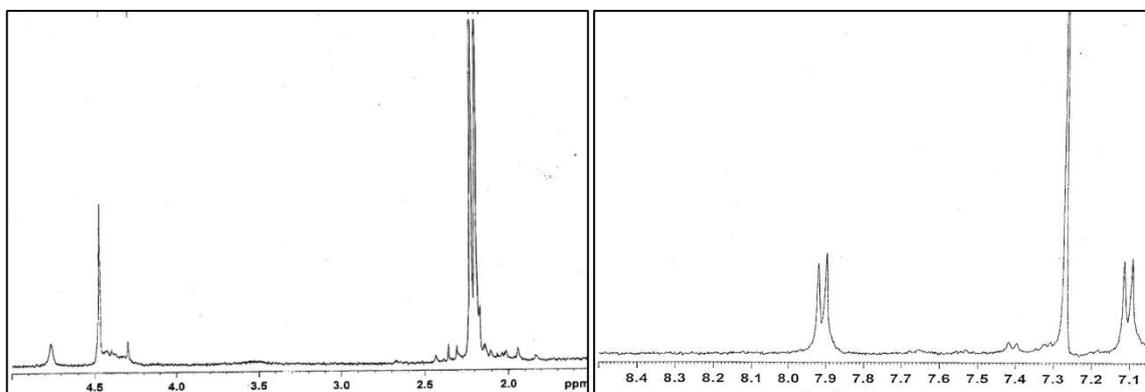
1) characterization of the synthesized compounds

the azo-dimer 5a-g exhibited medium IR absorption near 3000cm^{-1} (C-H , aromatic) and near (3134 cm^{-1}), (C-H , aliphatic) the later being stronger as the alkyl chain of the alkoxy group is longated (5e-g) .strong absorption near (1599 cm^{-1})and (1556 cm^{-1}) (C=C)and(N=N) and a strong band at (1222 cm^{-1}) (C-O-C).

The $^1\text{H-NMR}$ data for the compound (CDCl_3): (Fig.1)for (4) show two signals each singlet representing 12 proton at ($\delta=2.1,2.2$) represent methyl groups in the terminal benzene rings and triplet signals represent (2 proton) in the site ($\delta=4.35$) belong to a group ($-\text{OCH}_2$) ether and singlet signal Represent (1 proton) belonging to the group ($-\text{OH}$) at ($\delta=4.8$) and two signals each represent (4 proton) at ($\delta=7.1,7.9$) belonging to two benzene ring in the middle the compound (a5)shows same as the previous signals except for the appearance of mono signal belonging to a group ($-\text{OCH}_3$) Represent (3 proton) at ($\delta=3.7$) and the disappearance of a signal group ($-\text{OH}$) at ($\delta=4.8$) .



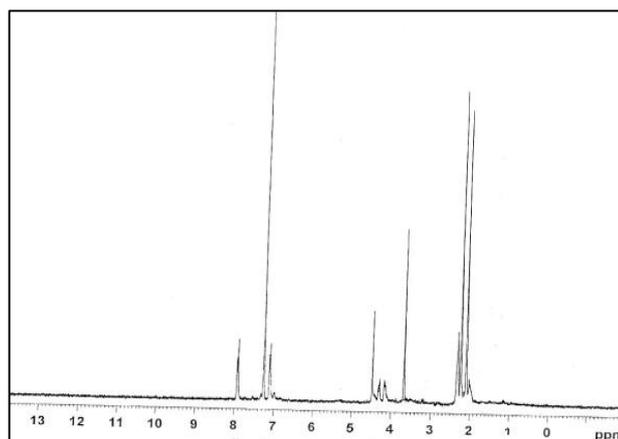
a



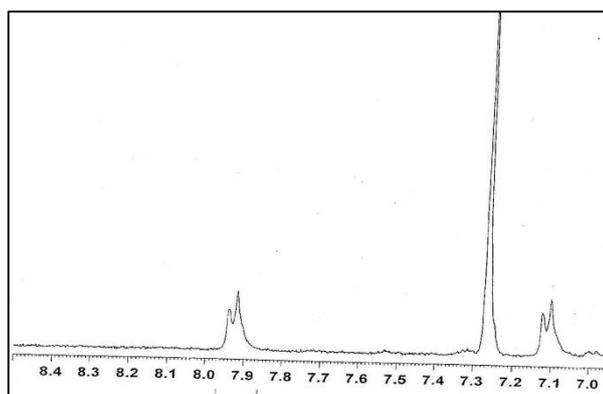
b

c

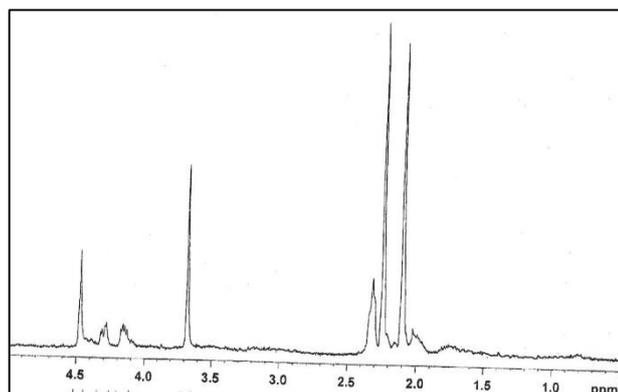
Fig (1).H.NMR Sptro(a,b,c) for (4)



a



b



c

Fig2.H.N.M.R Spectro(a,b,c) for (a5)

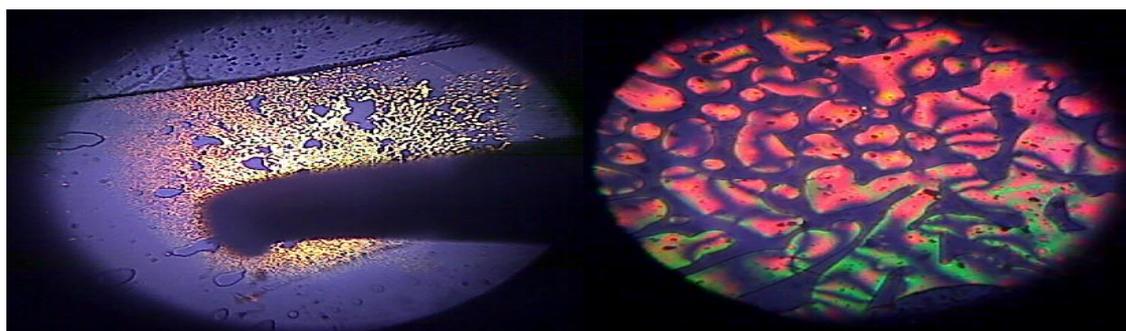
The synthesized azo-dimers had satisfactory elemental analyses and are consisted with those expected (Table1)

Table(1) .Elemental analytical data (of the liquid crystals)

compound	Molecular Formula	C%	H%	N%
5	C ₃₄ H ₃₈ N ₄ O ₄	72.056	6.228	9.301
5a	C ₃₆ H ₄₂ N ₄ O ₄	72.012	7.097	9.787
5b	C ₃₈ H ₄₆ N ₄ O ₄	73.193	7.330	9.127
5c	C ₄₀ H ₅₀ N ₄ O ₄	73.618	8.897	7.790
5d	C ₄₂ H ₅₄ N ₄ O ₄	74.693	7.726	8.185
5e	C ₄₄ H ₅₈ N ₄ O ₄	73.651	7.843	7.809
5f	C ₄₆ H ₆₂ N ₄ O ₄	75.693	8.726	7.785
5g	C ₄₈ H ₆₆ N ₄ O ₄	75.044	8.102	7.805

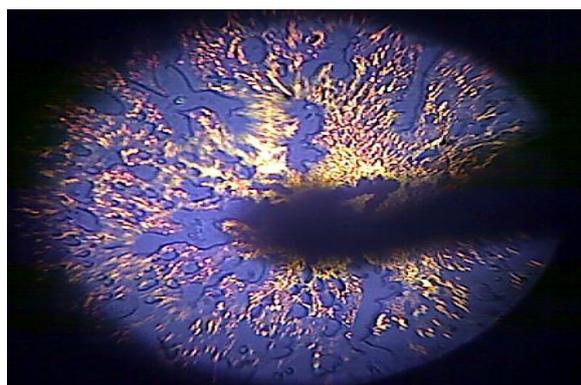
Mesomorphic behavior 2)

The identification of the mesophases and determination of phase transition temperatures were achieved with the help of polarizing optical microscopy (pom) . The sample placed between a clean an treated glass slide and a cover slip . The mesophase assignment was based on the observation of birefringence and fluidity when examined under pom .The liquid crystalline texture of the title compounds and phase identification was made by comparing the observed textures with those reported the literature [12,13] . All the compounds except (n=1) exhibited enantiotropic nematic phase with homogenous and schlieren textures (picture 1,2,3)the members (n=4-7) show smectic C phase (picture 4,5,6,7) in addition to nematic phase .when compared with low molar mass, the later show smectic monotropic phase because of the broadening groups(tetra methyl) in the substituted benzene ring[14].

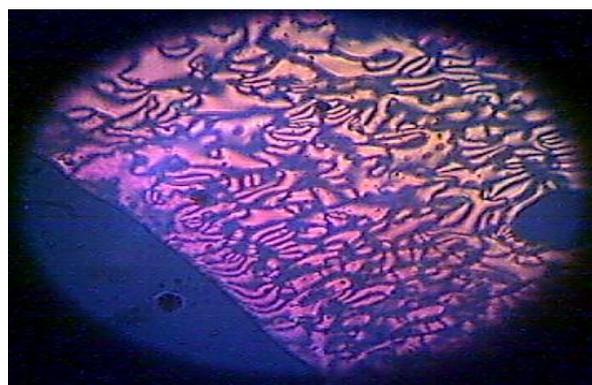


**Picture(1). nematic phase n=4
When heated 231C° degree**

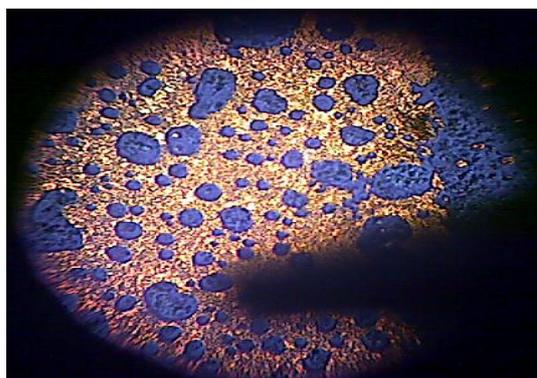
**Picture(2). nematic phase n=6 When
heated 211C° degree**



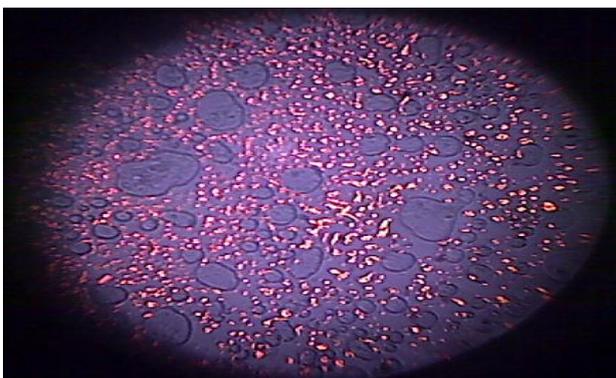
Picture (3). nematic phase $n=6$ When heated 238°C degree



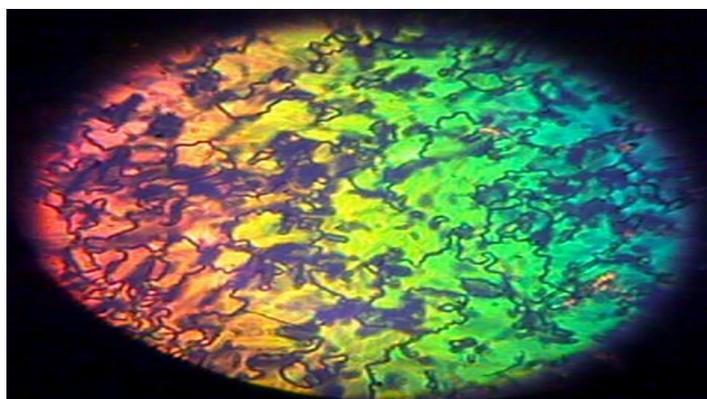
Picture (4). homogenous and schlieren textures $n=4$ When heated smectic C phase 200°C degree



Picture (5). smectic C phase $n=6$ when heated 193°C degree



Picture(6). smectic C phase $n=5$ when heated 201°C degree



Picture(7). smectic C phase $n=7$ When heated 207°C degree

Table (2): phase transitions C° for the series 5a – g (n=1-7)

n	Cr-Sc	Sc-N	N-Is	T _N Δ	T _{Sc} Δ
1	193
2	187	215	28
3	173	205	32
4	171	225	233	8	54
5	180	231	248	17	51
6	173	201	242	41	28
7	164	218	256	38	54

Cr: crystal , N: nematic , I: isotropic,Sc,SmecticC

A plot of the transition temperature against the number of carbon atoms on the terminal alkoxy chain for the series 5a-g (n=1-7) is shown in Figure 2. The plot shows typical mesogenic behavior. The nematic – isotropic transition temperature curve is going up with some indication of odd-even effect.

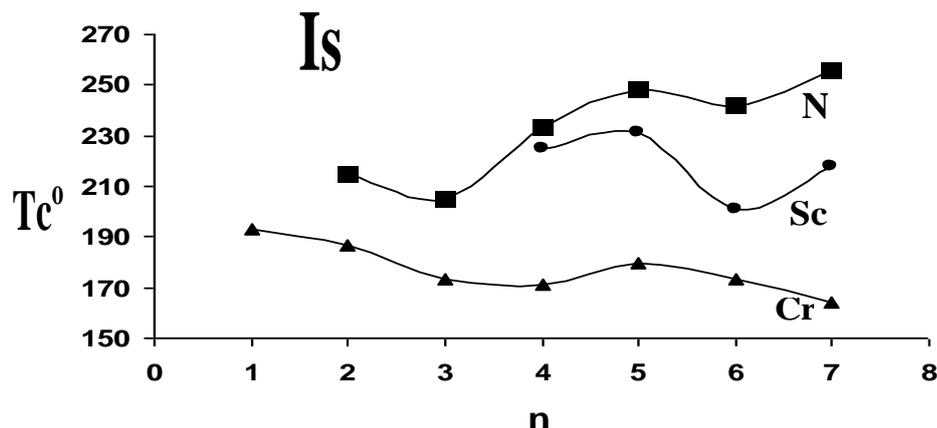


Fig (3).plot of phase transition temperature against the number of carbon atoms (n) in alkoxy chain

Conclusion

The paper presents synthesis and liquid crystalline behavior of some azo symmetric dimers compounds which are characterized by FT-IR, ¹HNMR and CHN-analysis. All reported compounds presented enantiotropic liquid crystalline properties except (n=1) the members (n=4-7) show smectic C phase in addition to nematic phase. The dimers indicate that their polymers may show mesomorphic properties also.

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تحضير مركبات الأزو كبلورات السائلة

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تاريخ الاستلام : 2013\9\15

ساجدة هادي رضا ونور محمود عبد الحسين
قسم الكيمياء ، كلية التربية للبنات ، جامعة الكوفة ، الكوفة / العراق .

الخلاصة

تم تحضير سلسلة من الدايمرات المتماثلة

α,β - Bis(4-n-alkoxy-2,3,5,6- methyl-4-oxy-Azo-benzene)ethane (n=1-7).

وشخصت بواسطة طيف IR ، $^1\text{H-NMR}$ وتحليل CHN وعينت الصفات البلورية السائلة بواسطة المجهر الضوئي المستقطب

جميع الاعضاء اظهرت خواص ميزومورفية ماعدا العضو (n=1) . الاعضاء (n=2,3) اظهرت طور نيماطي ايناشوتروبي

نقي بينما الاعضاء (n=4-7) اظهرت طور سمكتي C ايناشوتروبي بالاضافة الى طور نيماطي ايناشوتروبي.