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Synthesis and Characterization of Dimers with Azo and Salicylaldimine as Linking Group

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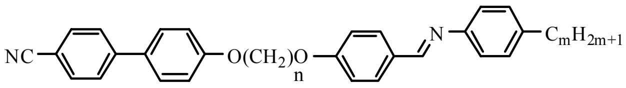
In the present study, a series of Schiff's bases: **1a-1d**; N,N'-*bis*-[2-hydroxy-5-(4'-*n*-decyloxy)phenylazobenzylidene]-4,4'-diamino diphenylmethane (DDMO-n) (*n*-alkoxy = decyloxy, undecyloxy, dodecyloxy, tetradecyloxy) and N,N'-*bis*-[2-hydroxy-5-(4'-*n*-decyloxy)-benzylidene]-4,4'-diamino diphenyl methane (16aldddm) homologues have been synthesized and characterized by IR, NMR spectroscopy and elemental analyses. The mesomorphic character of these compounds was mainly studied by using polarizing microscope equipped with a heating and cooling stage. Electrochemical reductions were studied by use of cyclic-voltammetric technique. These compounds gave one peak and are irreversible in nature in presence of tetra butyl ammonium bromide (TBAB) as supporting electrolyte. The electrochemical reductions of imines group were found to be diffusion controlled. All the compounds showed good biological results.

Key Words: Dimers, Azo, Salicylaldimine.

INTRODUCTION

Liquid crystal (LC) symmetric dimers or non-symmetric dimers are formed, respectively, when two structurally identical or different mesogenic entities are covalently interlinked *via* a flexible spacer[1-5]. These nonconventional molecular architectures, especially achiral non-symmetric dimers, have been attracting much attention as they exhibit a notably different phase behaviour when compared to their symmetric analogues. For example, the symmetric dimers with short and intermediate spacer lengths show exclusively the smectic behaviour whereas higher members exhibit nematic behaviour only[6-8]. In contrast, for example, the well studied CBOnO.m series of non-symmetrical dimers (Chart 1; n and m indicate the length of the spacer and terminal tail respectively)[2,4] display smectic behaviour for short and longer spacer lengths but not for intermediate lengths[2,4]. This unique feature arises from the different types of structures (interdigitated or intercalated) of the smectic phase formed by the distinct intermolecular interactions among the cores, terminal chain and the spacer parts. Of course, the dependence of smectic behaviour on the relative lengths of the spacer also holds good for other nonsymmetric dimers featuring electron rich/deficient mesogenic entities[1]. Inspired by these observations, we have recently reported new dimers in which the Schiff's base unit of CBOnO.10

was replaced with another electron rich moiety, the salicylaldimine core, with a view to understand the structure-property relationship[9a]. Interestingly, two of the five dimers, synthesized exhibit the biaxial smectic A (SmAb) phase.



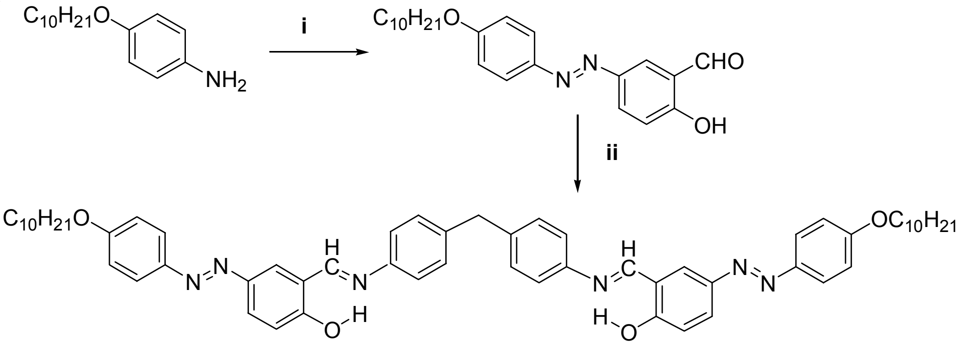
CBOnO.m; n = 3-12 , m = 0-10

Chart 1. Molecular structure of the most extensively studied nonsymmetric dimers (CBOn.Om series; see refs. 2 and 4)

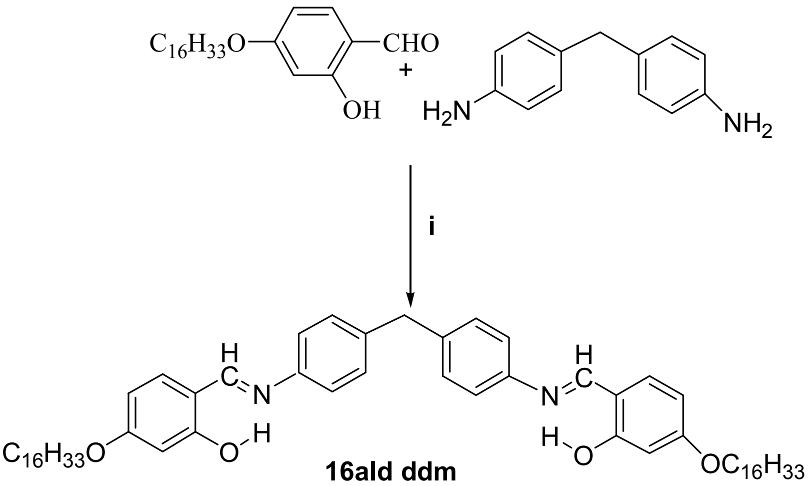
Liquid crystal dimers can be broadly classified into two categories; symmetric and non-symmetric. In the former class of dimers the molecular structures of mesogenic entities are identical whereas in the latter case they are different. These two groups can be further sub-divided according to the molecular shape geometry of the two-mesogenic entities. As is well known, metal containing liquid crystals (metallomesogens) are a novel class of materials that combine the properties of anisotropic fluids and the features of metals (such as magnetic and electronic properties)[10]. A variety of metallomesogens, including polymers[11] have been realized with a view to understand the structure-property correlations. Surprisingly, only a few metal-containing linear oligomers are known[12]. For example, we have recently reported the synthesis and mesomorphism of the first examples of optically active (cholesterol-based) dimeric bidentate ligands and their Cu(II) and Pd(II) complexes[13]. Conversely, to the best of our knowledge, achiral metal-containing oligomeric liquid crystals and in particular, metallomesogens derived from bidentate dimeric ligands have not been reported *hitherto*. In this context, the aforementioned[9a] dimeric molecules are promising as they possess an electron rich salicylaldimine core[14] that forms (N-O) chelates with many metals. Here we report the details of the synthesis and characterization of metal-organic systems obtained by chelating achiral dimeric bidentate ligands (**Scheme-I** and **II**). For convenience, we denote the ligands by mnemonics DDMO-n and 16aldmm-n, respectively.

Schiff's base and their metal complexes have been reported to possess important biological, catalytic activity and also oxygen carriers. For the purpose of antimicrobial and antifungal screening 4 bacterial strains and one fungus *i.e.*, *Staphylococcus aureus, Bacillus subtilis, Proteus vulgaris, Pseudomonas aruginosa* and *Candida albicans* were chosen. *Staphylococcus aureus, Bacillus subtilis* are a gram-positive organism while *Proteus vulgaris, Pseudomonas aeruginosa* are a gram negative one. A wide range of techniques can test antimicrobial and antifungal activity of a drug or a test compound.

Schiff base complexes of cobalt and nickel play an important role in many electrocatalytic processes. Nickel complexes have been recognized as powerful catalysts in the chemical and electrochemical reduction of alkyl halides.



Scheme-I: Reagents and conditions: i = HCl, $NaNO_2$, H_2O, 0-5 ºC, NaOH, H_2O and salicylaldehyde; ii. 4,4′-diaminodiphenylmethane, abs EtOH, cat AcOH, D, 3 h



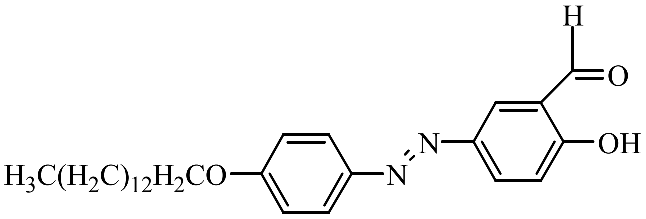
16ald ddm

Scheme-II: Reagents and conditions: i. abs EtOH, cat AcOH, heat 3 h

EXPERIMENTAL

Solvents used in reactions were purified and dried by standard methods. The crude samples were purified by column chromatographic technique using either silica gel (400 mesh) or neutral aluminium oxide as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselge 60, F_{254}). The absorption spectra were recorded on a Perkin-Elmer Lambda 20 UV-Vis spectrometer. IR spectra were recorded using Perkin-Elmer Spectrum 1000 FT-IR spectrometer. ^{1}H NMR spectra were recorded using either a Bruker AMX-400 (400 MHz) or a Bruker Aveance series DPX-200 (200 MHz) spectrometer and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard. Elemental analyses were carried out using a Eurovector EA3000 series CHNOS analyzer. Mass spectra were recorded on a Jeol-JMS-600H spectrometer in FAB + mode using 3-nitrobenzyl alcohol as a liquid matrix. The identification of the mesophases and the transition temperatures of the target molecules were determined using a polarizing microscope (Leitz DMRXP) in conjunction with a programmable hot stage (Mettler FP90). The melting point of the crystalline compounds to their liquid state was determined with help of the above-mentioned microscope and hot stage. The enthalpies of the phase transition were measured using a differential scanning calorimeter (Perkin-Elmer DSC7) that was calibrated using indium as standard prior to use. The thermograms were recorded for two heating and cooling cycles at a rate of 5 ºC/min.

Synthesis of 2-hydroxy-5-(4'-*n*-tetradecyloxy)phenylazobenzaldehyde(14n$_2$)



To a solution of 30 mL of water containing hydrochloric acid (6.85 mL, 4.4 M, 0.03 mol) 4-*n*-tetradecyloxyaniline (0.01 mol) was added slowly to form a clear solution. To the resulting solution, which was stirred and cooled to 0 °C, an aqueous cold solution of $NaNO_2$ (0.76 g, 0.011 mol) was added drop wise maintaining the temperature of the reaction mixture at 0-5 °C, to yield the diazonium chloride. It was subsequently coupled with salicylaldehyde (1.22 g, 0.01 mol), which was dissolved in 11.5 mL of aqueous 2 N NaOH (0.92 g, 0.023 mol) solution. The reaction mixture was stirred for 1 h at 0-5 °C and then allowed to warm slowly to room temperature with stirring for over 1 h. The resulting yellow precipitate was filtered, washed with water several times. The crude product was dissolved in CH_2Cl_2 dried over Na_2SO_4. After removal of the solvent under reduced pressure the sample was recrystallized from ethanol to give a single spot on thin layer chromatography. Yield 90 %. m.p. 124.7 °C.

IR: (KBr pellet, cm^{-1}): 3100 (ν_{OH}), 2955, 2919 (ν_{aCH}, methyl or methylene), 2849, 2873 (ν_{sCH}, methyl or methylene), 1673 ($\nu_{C=O}$), 1506 ($\nu_{C=C}$); 1287 (ν_{O-C}). ^1H NMR: (400 MHz, $CDCl_3$): δ 0.90 (t, 3H, *J* = 6.3 Hz, CH_3), 1.26-1.44 (m, 28H, $(CH_2)_4$), 4.00 (t, 2H, *J* = 6.3 Hz, CH_2O), 6.41 (d, 1H, *J* = 2.3 Hz, Ar), 6.52 (dd, 1H, *J* = 2.0 and *J* = 8.6 Hz, Ar), 7.41 (d, 1H, *J* = 8.6 Hz, Ar), 9.69 (s, 1H, CHO) and 11.48 ((s, 1H, OH).

The intermediate aldehydes 4-*n*-hexyloxysalicyladehyde, 4-*n*-octadecyloxysalicyl adehyde are synthesized following the procedure adopted for 4-*n*-hexadecyloxy salicyladehyde.

Synthesis of N,N'-*bis*-[2-hydroxy-5-(4'-*n*-decyloxy)phenylazobenzylidene]-4,4'-diamino diphenylmethane (DDMO10): An ethanolic solution (20 mL) of 2-hydroxy-5-(4'-*n*-decyloxy) phenylazo benzaldehyde (2 mmol) was added to an ethanolic solution of 4,4'-diaminodiphenylmethane (1 mmol). The solution mixture was refluxed with a few drops of glacial acetic acid as catalyst for 3 h to yield the yellow Schiff's base N,N'-*bis*-[2-hydroxy-5-(4'-*n*-decyloxy)phenylazo benzylidene]-4,4'-diaminodiphenylmethane (**2**).The precipitate was collected by filtration and recrystallized several times from absolute ethanol to give a pure compound, Yield 89 %.

Elemental analysis: Elemental analysis calculated for $C_{59}H_{70}N_6O_4$, C, 76.42; H, 7.61; N, 9.06; found C, 76.45; H, 7.55; N, 9.07. The experimental values of C, H and N are found to be in good agreement with theoretical values.

IR analysis (KBr pellet, data in cm^{-1}) 3436 (ν_{OH}), 2919 (ν_{aCH}, methyl or methylene), 2850 (ν_{sCH}, methyl or methylene), 1619 ($\nu_{C=N}$), 1584 ($\nu_{C=C}$); 1501 (N=N) and 1246 (ν_{O-C}). ^{1}H NMR data: (δ values in ppm and J values in Hz). 13.85 (s, OH, 2H, H8), 8.75 (s, CH=N, 2H, H9), 7.99-8.03 (m, 4H, Ar), 7.98 (d, J = 9.08 Hz, 4H, Ar), 7.20-7.80 (m, 4H, Ar), 7.11 (d, J = 9.08 Hz, 4H, Ar) 7.01 (d, J = 9.0 Hz, 2H, Ar), 4.20 (s, 2H, Ar-CH$_2$-Ar) 4.07 (t, J = 6.6 Hz, 4H, -CH$_2$-), 1.2 to 1.8 (m, 32H,-CH$_2$-), 0.88 (t, J = 6.6 Hz, 6H, -CH$_3$-).

DDMO11: IR analysis (KBr pellet, data in cm^{-1}) 3436 (ν_{OH}), 2919 (ν_{aCH}, methyl or methylene), 2850 (ν_{sCH}, methyl or methylene), 1619 ($\nu_{C=N}$), 1584 ($\nu_{C=C}$); 1501 (N=N) and 1246 (ν_{O-C}). ^{1}H NMR data: (δ values in ppm and J values in Hz). 13.89 (s, OH, 2H, H8), 8.75 (s, CH=N, 2H, H9), 7.99-8.03 (m, 4H, Ar), 7.98 (d, J = 9.08 Hz, 4H, Ar), 7.20-7.82 (m, 4H, Ar), 7.11 (d, J = 9.08 Hz, 4H, Ar) 7.03 (d, J = 9.0 Hz, 2H, Ar), 4.20 (s, 2H, Ar-CH$_2$-Ar) 4.07 (t, J = 6.6 Hz, 4H, -CH$_2$-), 1.2 to 1.8 (m, 32H, -CH$_2$-), 0.88 (t, J = 6.6 Hz, 6H, -CH$_3$-).

DDMO12: Elemental analysis: Elemental analysis calculated for $C_{59}H_{70}N_6O_4$, C, 76.95; H, 8.00; N, 8.55, found C,76.78; H, 7.27; N, 8.23. The experimental values of C, H and N are found to be in good agreement with theoretical values.

IR analysis (KBr pellet, data in cm^{-1}) 3436 (ν_{OH}), 2919 (ν_{aCH}, methyl or methylene), 2850 (ν_{sCH}, methyl or methylene), 1619 ($\nu^{C=N}$), 1584 ($\nu_{C=C}$); 1501 (N=N) and 1246 (ν_{O-C}). ^{1}H NMR data: (δ values in ppm and J values in Hz). 13.85 (s, OH, 2H, H8), 8.75(s, CH=N, 2H, H9), 7.99-8.03 (m, 4H, Ar), 7.98 (d, J = 9.08 Hz, 4H, Ar), 7.20-7.80 (m, 4H, Ar), 7.11 (d, J = 9.08 Hz, 4H, Ar) 7.01 (d, J = 9.0 Hz, 2H, Ar), 4.20 (s, 2H, Ar-CH$_2$-Ar) 4.07 (t, J = 6.6 Hz, 4H, -CH$_2$-), 1.2 to 1.8 (m, 32H,-CH$_2$-), 0.88 (t, J = 6.6 Hz, 6H, -CH$_3$-).

DDMO14: Elemental analysis: Elemental analysis calculated for $C_{59}H_{70}N_6O_4$, C, 77.42; H, 8.34; N, 8.09; found C, 77.01; H, 8.38; N, 9.54. The experimental values of C, H and N are found to be in good agreement with theoretical values.

IR analysis (KBr pellet, data in cm^{-1}) 3436 (ν_{OH}), 2919 (ν_{aCH}, methyl or methylene), 2850 (ν_{sCH}, methyl or methylene), 1619 ($\nu_{C=N}$), 1584 ($\nu_{C=C}$); 1501 (N=N) and 1246 (ν_{O-C}). ^{1}H NMR data: (δ values in ppm and J values in Hz). 13.85 (s, OH, 2H, H8), 8.75 (s, CH=N, 2H, H9), 7.99-8.03 (m, 4H, Ar), 7.98 (d, *J* = 9.08 Hz, 4H, Ar), 7.20-7.80 (m, 4H, Ar), 7.11 (d, *J* = 9.08 Hz, 4H, Ar) 7.01 (d, *J* = 9.0 Hz, 2H, Ar), 4.20 (s, 2H, Ar-CH_2-Ar) 4.07 (t, *J* = 6.6 Hz, 4H, -CH_2-), 1.2 to 1.8 (m, 32H,-CH_2-), 0.88 (t, *J* = 6.6 Hz, 6H, -CH_3-).

Synthesis of N,N'-*bis*-[2-hydroxy-5-(4'-*n*-decyloxy)benzylidene]-4,4'-diamino diphenyl methane (16aldddm): The synthetic procedure is described earlier.

Elemental analysis: Elemental analysis calculated for $C_{59}H_{86}N_2O_4$, C, 79.86; H, 9.77; N, 3.16 found C, 78.61; H, 10.56; N, 4.15. The experimental values of C, H and N are found to be in good agreement with theoretical values. IR analysis (KBr pellet, data in cm^{-1}) 3368 (ν_{OH}), 2918 (ν_{aCH}, methyl or methylene), 2850 (ν_{sCH}, methyl or methylene), 1627 ($\nu_{C=N}$), 1599 ($\nu_{C=C}$), 1246 (ν_{O-C}). ^1H NMR data: (δ values in ppm and *J* values in Hz). 13.75 (s, OH, 2H, H8), 8.50 (s, CH=N, 2H, H9), 7.23 (d, *J* = 8.5 Hz, 4H, Ar), 7.21 (d, *J* = 8.5 Hz, 4H, Ar), 7.16 (d, *J* = 8.8 Hz 2H, Ar), 6.54 (d, *J* = 2.1, 9.8 Hz, 2H, Ar), 6.48 (d, *J* = 2.1 Hz, 4H, Ar), 3.99 (t, 6.5Hz, 4H, -OCH_2-), 1.20 to 1.80 (m, 56H, -CH_2-), 0.89 (t, 6.6 Hz, 6H, -CH_3).

RESULTS AND DISCUSSION

Thermal microscopy and differential scanning calorimetry of 16aldddm: The transition temperatures are detected by differential scanning calorimetry and liquid crystalline behaviour is observed by thermal microscopy. The compounds synthesized, observed transition temperatures by DSC and thermal microscopy along with enthalpy values. The detailed description of experimental observations is presented for a representative sample 16aldddm.

Thermal microscopy texture of 16aldddm: The virgin sample on heating exhibited three phase transitions at 109.5 °C (88.9 J/g), 124.2 °C (1.43 J/g), 151.8 °C (4.78 J/g) in the heating cycle and at 124.6 °C (14.97 J/g) in the cooling cycle. Upon further cooling from isotropic, the schlieren texture becomes dressed by parallel lines. These lines have been interpreted as layer undulations caused by stresses due to thermal contraction and the contraction may be exceptionally large because of large increase in tilt upon cooling in SmX1 phase. Such sudden increase in tilt angle leading to layer contraction at the onset of smectic phase is observed. On further cooling smectic X_2 phase with four brushes is observed. These undulation lines did not disappear even at room temperature.

Moreover a majority of banana liquid crystalline materials are the Schiff base derivatives, while a major drawback of these materials is their limited thermal, hydrolytic and photochemical stability. However in the present case the hydroxyl group *ortho* to imine linkage not only stabilizes to the external stimuli but also stabilizes the molecule through the participation of an intra and/or inter molecular H-bonding thereby promoting non covalent self-assembly. The helical assemblies are possibly due to the intra and/or inter molecular H-bonding promoted supramolecular structures to exhibit banana liquid crystalline phases. As the compounds are extended *bis* salen derivatives, can be used as ligands for complexation with a C_2 symmetry. As *bis* (salicylideneaminato)-metal Schiff base complexes are found to be interesting candidates to exhibit NLO properties, the addition of liquid crystalline property may add to its application potential. The photoactive azo group in the molecule can induce the changes in photo-physical properties. It shows most of the synthesized compounds were found to be good antibacterial and antifungal agents due to aromaticity and conjugation of molecules.It is shown in Table-1.

TABLE-1
ANTIMICROBIAL ACTIVITY OF COMPOUNDS AGAINST *S. aureus*, *B. subtilis*, *P. vulgaris*, *P. aeruginosa* AND *C. albicans* (ZONE OF INHIBITION IN mm)

Compound	*S. aureus*	*B. subtilis*	*P. vulgaris*	*P. aeruginosa*	*C. albicans*
16aldddm	18	15	16	11	13
DDMO10	12	14	12	16	12
DDMO11	13	12	12	13	11
DDMO12	R	R	8	R	9
DDMO14	R	R	7	R	9
Standard	30	26	26	36	15

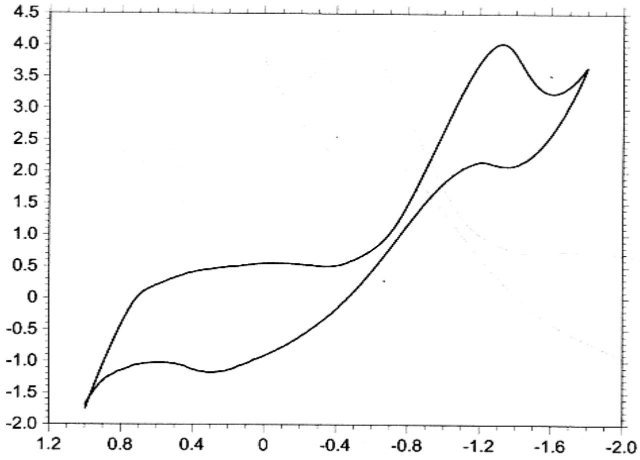
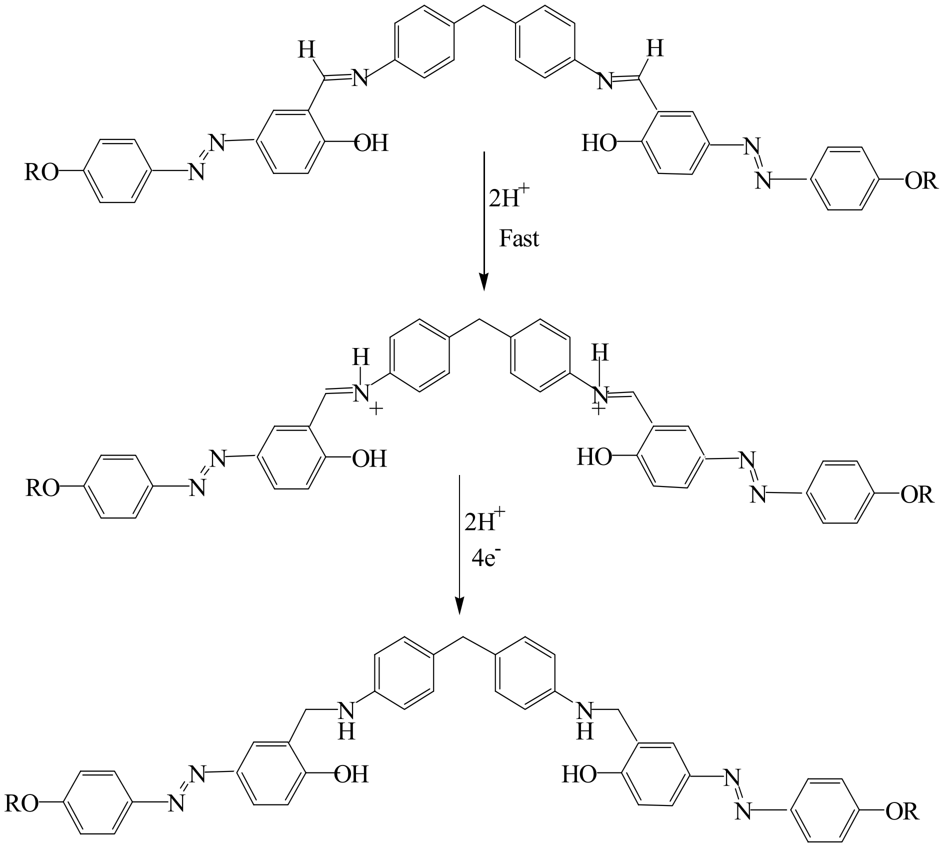


Fig. 2. Cyclic voltammogram of DDMO10 at n = 0,C = 1 × 10^{-3}

The lack of conjugation between the two iminic sides of the molecule makes the voltammetric potential of DDMOn much simpler than that of conjugated compounds. DDMOn exhibits in fact only one irreversible reduction peak with the range of Ep = -0.99 to = -1.33 V at ν = 0.1 V/s and c = 0.003 M. Variation of the scan rate up to 500 V causes no substantial modification of the voltammetric behaviour. The current function, Ip/√ν is independent of the scan rate. It confirms the diffusion controlled nature of the electrochemical reduction of DDMOn. In the presence of acetic acid pre-peak appeared which is more positive than the main reduction potential. The appearance of a pre-peak in the voltammetric reduction of DDMOn in the presence of acetic acid may also relate to its basic properties. In the presence of acetic acid protonation of the imine may take place to give an iminium ion, the reduction potential of which is expected to be more positive than that of the starting imines. The observed pre-peak may be attributed to the reduction of the iminium ion. The addition of 1 equivalent Bu_4NOH (tetra butyl ammonium hydroxide) shifts the original peaks towards more negative potential side. This peak is to be attributed to the reduction of the monodissociated conjugated base. Addition of a further equivalent of base eliminates this peak. This reduction of the doubly dissociated dianion is beyond the cathodic discharge. So that in the presence of 2 equivalents of Bu_4NOH no peaks are observed. The electrode reduction scheme of DDMOn is given in **Scheme-III**. While increasing alkyl chain length there is not much effect on reduction potential. Cyclic voltammetric peak parameters for the reduction of DDMO10 on platinum electrode containing 1×10^{-3} (M) and 0.1 M TBAB are given in Fig. 3. Reductions potential for all compounds of these types are given in Table-2.



$R=C_nH_{2n+1}$, n=10,11,12,14,16

Scheme-III: Electrochemical reduction of DDMO-n series

Fig. 3. Anticrobial activity of synthesized compounds (4, 5 and 7) against *S. aureus*

TABLE-2
VALUES OF PEAK POTENTIAL (-Ep, V) AND
PEAK CURRENT (Ip, µA) OF DDMOn COMPOUNDS

Compound	Ip (µA)	-Ep (V)
DDMO11	4.63	0.99
DDMO12	4.33	1.23
DDMO14	4.35	1.19
DDMO16	4.21	1.21
DDMO18	4.23	1.33

Conclusion

An attempt has been made to understand the mesomorphic behaviour of some symmetrical bent-core compounds. These compounds were synthesized using biphenyl methane used as a central core. Indeed, contrary to resorcinol, the central part based on isophthalic acid is rigid due to the conjugation and the first conformational freedom is rejected at the level of the intermediate rings of the branches. Neverthless, this study shows that a a suitable choice of linking groups and lateral substituents can induce mesophases with electro optic properties. Synthesized compounds are showing electrochemical reduction property. Most of the synthesized compounds are biological active in nature.

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