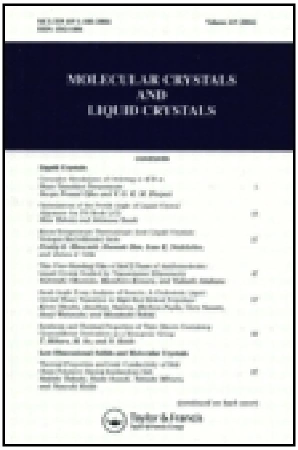

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Novel Nonlinear Optical Chromophores Exhibiting Mesomorphism

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NOVEL NONLINEAR OPTICAL CHROMOPHORES EXHIBITING MESOMORPHISM

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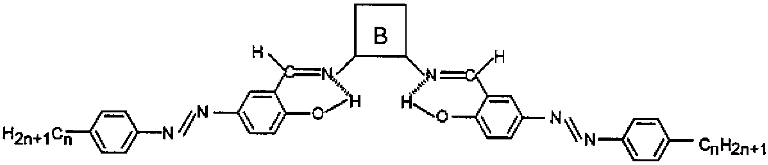
The bent-shaped tetra dentate Schiff's base ligands N,N′-bis [5-(4′-n-alkyl)-phenylazosalicylidene] alkyldiamine $H_2L(n = 12)$ based on 1,1-, 1,2-, and 1,3-diamines viz., urea, diaminomaleonitrile, 1,2-phenylenediamine, and 4-nitro-1,3-phenylenediamine with the following molecular structure:



where B is the bridging group 1,1-diamine ex: urea; and 1,2-diamine ex: diaminomaleonitrile and 1,2-phenylenediamine and 1,3-diamine ex: 4-nitro-1, 3-phenylenediamine were synthesized and characterized. All the compounds exhibit liquid crystalline properties.

Keywords: Schiff's bases; liquid crystals; banana-shaped molecules; nonlinear chromophores

INTRODUCTION

During the last century, rodlike molecules have been dominant among those exhibiting crystalline behavior that find applications in display devices. In the late 1970s the discovery of metallomesogens and disclike molecules capable of forming columnar liquid crystalline phases apart from conventional liquid crystalline phases have opened up new areas of research. Furthermore, in 1996 the discovery of ferroelectric characteristics in bent-shaped molecules **1**, which not only exhibit liquid crystalline

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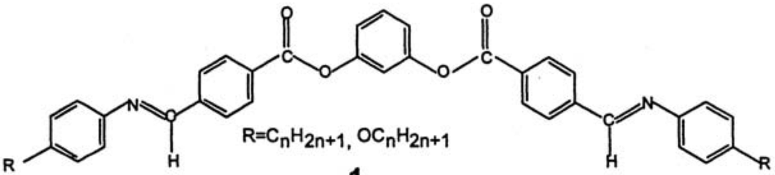
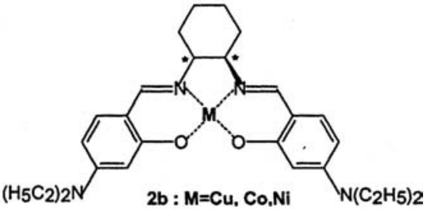
Address correspondnce to N. V. S. Rao, E-mail: nvsrao@sancharnet.in polymorphism but also distinct switching characteristics, has motivated many of the liquid crystalline scientists to design and synthesize new materials for possible potential applications in emerging opto-electronic technologies. These achiral V-shaped, bent-shaped or banana-shaped molecules (**1**), possessing C_{2V} symmetry and aided by smectic stacking of molecules with hindered rotation, exhibit polar order. Consequently, a net spontaneous polarization, and hence ferroelectricity (or anti-ferroelectricity), has become the resultant material properties. Furthermore, the polar order is equivalent to a noncentrosymmetric arrangement of molecules, and hence these molecules are also of interest to exhibit second order nonlinear optical (NLO) properties characterized by large first hyperpolarizability (β).



R=C_nH_{2n+1}, OC_nH_{2n+1}

1

2a : M = Ni,Cu,Zn

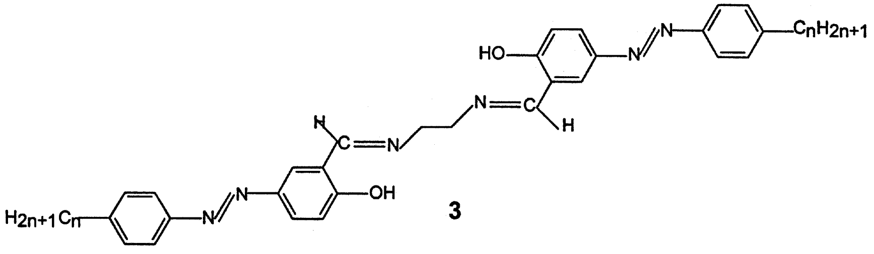


2b : M=Cu, Co,Ni

However, nonmesogenic organo-metallic compounds, possessing C_{2V} symmetry, derived from bis(salicylaldiminato)metal Schiff's base complexes (**2a** and **2b**) also exhibit large molecular hyperpolarizabilities [1a,1e]. Hence the synthesized NLO materials can be broadly classified into two categories viz., nonmesogenic organo-metallic compounds [1] and mesogenic organic compounds [2–6]. The crucial prerequisite for achieving large second order NLO response in any of the above materials is that the individual constituent molecule should possess a large molecular first order hyperpolarizability (β) response and then arrange into a noncentrosymmetric architecture [2]. Such molecular engineering for material optimization at the microscopic scale has been realized in recent reports on the metal complexes of a new Schiff's base ligand [1] based on the condensation of 1,2 diamines, prominent being diaminomaleonitrile (**2a**) (or 1,2-cyclohexyl (**2b**) or 1,2-phenylenediamine or its substituted ones) and

4-(diethyl amino) salicylaldehyde. The metal complexes derived from such ligands exhibit large values of hyperpolarizability (β) but do not exhibit liquid crystalline behavior. It is a subtle problem to match the requirements of a molecule possessing structural anisotropy to exhibit liquid crystalline behavior as well as the symmetry characteristics that lead to large hyperpolarizability values. The introduction of shape factor, which causes inevitable disruption to a molecule possessing structural anisotropy, leads to nonmesomorphic behavior. However, selective molecular engineering of such structures with a proper interplay of molecular structural anisotropy and the shape factor with required polarizability anisotropy has been achieved in banana- or bent-shaped liquid crystals which exhibit large spontaneous polarization (350–700 nC.cm^{-2}), P_S, values [4,7,8] that match the organo-metallic chromophores.

In attempting to devise a strategy for the synthesis of bent-shaped molecules, we reasoned that the organic fragments would need to be sufficiently anisotropic to match the perturbation produced in the form of a shape factor by the introduction of a bridging group between two organic fragments. Earlier attempts, to introduce aliphatic linking groups viz., 1,2-diaminoethane, 1,3-diaminopropane did not lead to liquid crystalline behavior or any NLO characteristics, with few exceptions [9]. Moreover, the development of liquid crystalline materials for optical switching has recently emphasized the role of photoisomerizing species, which exhibit a reversible isothermal phase transition. Recently, Ghedini et al. [10,11] reported nonmesomorphic N, N′-bis[-5-(4′-*n*-alkyl)phenylazosalicylidene]-alkyldiamines), based on 1,2-alkyldiamines (**3**). However the 4-n-alkoxy 5-substituted (N,N′-Salicylidenediamines) and their Nickel (II) complexes[10] (**4**), (n = 14, R = OC_6H_{13} or $OC_{18}H_{37}$) exhibit mesomorphism.



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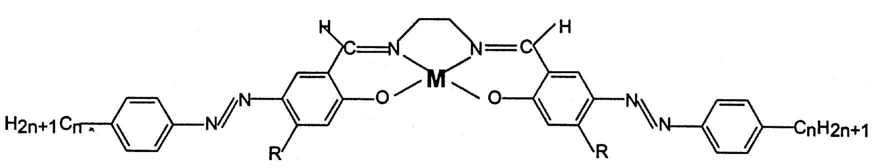


4

R = H or CH_3, M = Ni

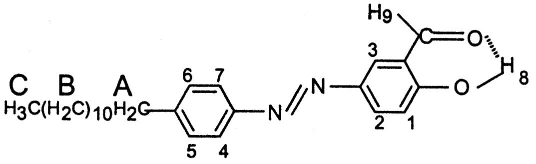
Further, the ligand molecules, despite the two-mesogenic alkyl phenol azo fragments, do not give a material that exhibits liquid crystalline behavior. The possible explanation for such behavior may be from the transoid N, N′ conformation which stabilizes a stepped molecular geometry that discourages mesomorphism. We believe that the augmentation of longitudinal polarizability along the long axis may favor mesomorphic behavior. Mesomorphic behavior exhibited by these nonmesomorphic ligands [10,11] upon complexation with either Copper(II) or Nickel(II) or Oxovanadium(IV), which promote the augmentation of longitudinal molecular polarizability, lends support to the above hypothesis.

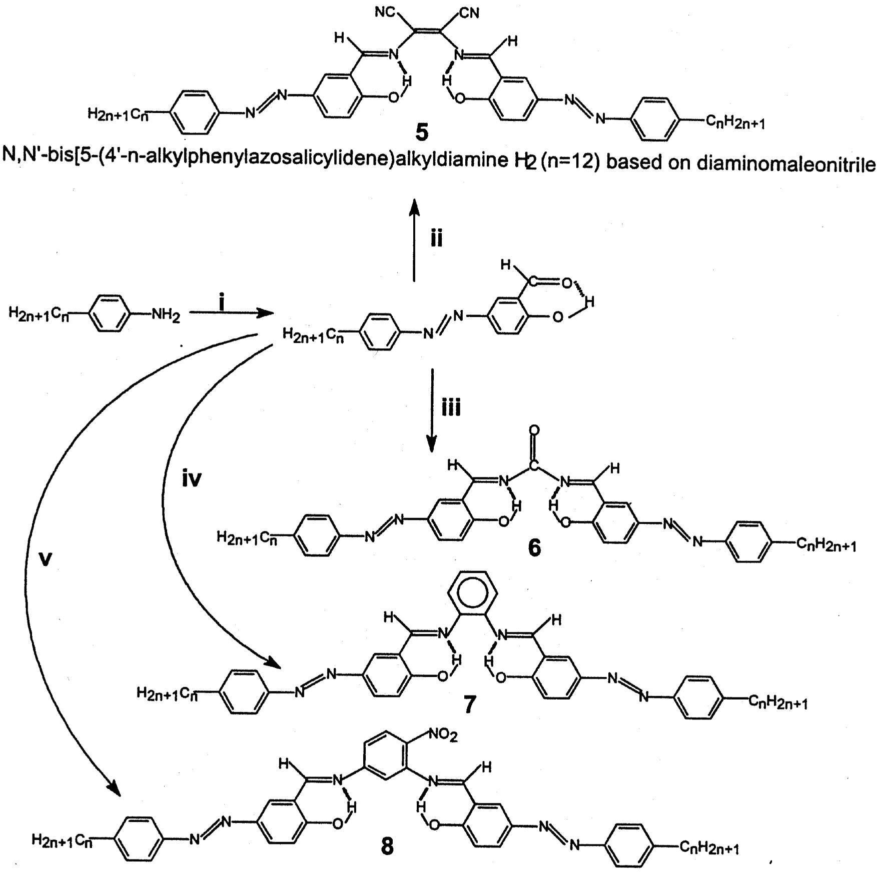
Furthermore, diaminomaleonitriles have never been used as building blocks either for mesogenic compounds or metallomesogens, even though 1,2- or 1,3-diamines are used in compounds exhibiting thermotropic liquid crystalline behavior. Hence condensing the basic building block of diaminomaleonitrile with two-photochromic mesogenic 4-n-dodecyl alkyl phenylazo salicylaldehydes gives rise to laterally fused structures, but at an angle with the bridge as a twin molecular mesogen with C_{2V} symmetry. We report here the synthesis and characterization of the liquid crystals derived from the condensation of 1,2-diamines (diaminomaleonitrile, 1,2-phenylenediamine), 1,1-diamine (urea), and 1,3-diamine (4-nitro-1,3-phenylenediamine) with [2-hydroxy-5-(4′-n-dodecyl) phenylazobenzaldehyde] to yield N, N′-bis-[2-hydroxy-5-(4′-n-dodecyl)-phenylazobenzylidene]-1,2-dicyanoethylene diamine (**5**) and other related compounds (**6**, **7** and **8**) for possible exploration of nonlinear optical property and photoisomerization characteristics.

EXPERIMENTAL

The synthesis of the materials was carried out following the procedures well documented in the literature and is presented in Scheme 1. All the compounds were characterized by elemental analysis, infrared (IR), and by conventional ^1H and ^{13}C NMR spectrarecorded, on JEOL-FX90 and Bruker WH-300, in $CDCl_3$ solutions with TMS as internal standard. The liquid crystalline properties were established using a Nikon Optiphot-2 polarizing microscope in combination with a Instec HS-ii hot stage with temperature controller, and the phase transitions are confirmed with Perkin-Elmer Pyris-1 differential scanning calorimeter. The phase transition temperatures are presented in Table I.

Synthesis of 2-hydroxy-5-(4′-n-dodecyl)phenylazobenzaldehyde

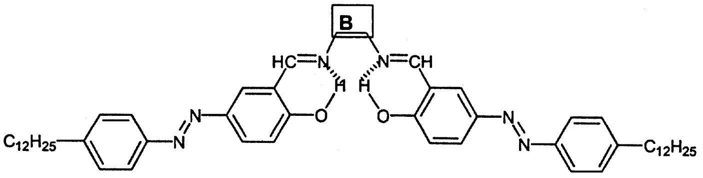




SCHEME 1 Synthetic route to compounds **5** to **8**. Reagents and conditions: i. HCl, $NaNO_2$, NaOH, H_2O, and salicylaldehyde. ii. diaminomaleonitrile, EtOH, few drops of glacial AcOH,Δ, 3 h. iii. urea, EtOH, few drops of glacial AcOH,Δ, 3 h. iv. 1,2-phenylenediamine, EtOH, few drops of AcOH,Δ, 3 h. v. 4-nitro-1,3-phenylenediamine, EtOH, few drops of AcOH,Δ, 3 h.

To a solution of 30 ml of H_2O containing hydrochloric acid (6.85 ml, 4.4 M, 0.03 mol), 4-n-dodecylaniline (2.6 g, 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 dropwise, 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 2N 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

TABLE I Molecular Structure and Phase Transition Temperatures of Compounds



Compound	Bridging group 	Phase transition temperatures and corresponding enthalpies ($J\cdot g^{-1}$) of compounds obtained from differential scanning calorimetry
5 DAMN12	**a**	$\mathrm{Cr}\ \underset{<40^\circ C}{\overset{80.5^\circ C(4.2)}{\rightleftharpoons}}\ \mathrm{LC2}\ \underset{60.5^\circ C(12.3)}{\overset{99.8^\circ C(10.8)}{\rightleftharpoons}}\ \mathrm{LC1}\ \underset{90.6^\circ C(10.1)}{\overset{118.1^\circ C(6.7)}{\rightleftharpoons}}$
6 UR12	**b**	$\mathrm{Cr}\ \underset{\dagger}{\overset{70.9^\circ C(1.8)}{\rightleftharpoons}}\ \mathrm{Cr1}\ \underset{70.3^\circ C(18.5)}{\overset{80.2^\circ C(19.3)}{\rightleftharpoons}}\ \mathrm{LC2}\ \underset{72.2^\circ C(8.0)}{\overset{82.4^\circ C(3.26)}{\rightleftharpoons}}\ \mathrm{LC1}\ \underset{92.3^\circ C(60.9)}{\overset{98.5^\circ C(60.9)}{\rightleftharpoons}}$
7 12PD12	**c**	$\mathrm{Cr}\ \underset{<40^\circ C}{\overset{57.9^\circ C(2.9)}{\rightleftharpoons}}\ \mathrm{LC2}\ \underset{54.9^\circ C(2.36)}{\overset{70.8^\circ C(7.0)}{\rightleftharpoons}}\ \mathrm{LC1}\ \underset{84.2^\circ C(0.65)}{\overset{94.5^\circ C(2.5)}{\rightleftharpoons}}$
8 134NPD12	**d**	$\mathrm{Cr}\ \underset{68.4^\circ C(7.7)}{\overset{72.2^\circ C(3.5)}{\rightleftharpoons}}\ \mathrm{LC3}\ \underset{76.6^\circ C(13.3)}{\overset{81.1^\circ C(28.5)}{\rightleftharpoons}}\ \mathrm{LC2}\ \underset{85.8^\circ C(1.2)}{\overset{81.6^\circ C(9.9)}{\rightleftharpoons}}\ \mathrm{LC1}\ \underset{88.0^\circ C(42.7)}{\overset{95.6^\circ C(30.8)}{\rightleftharpoons}}$

The values in parentheses are enthalpy in $J\cdot g^{-1}$.
(a) Diaminomaleonitrile.
(b) Urea.
(c) 1,2-phenylenediamine.
(d) 4-nitro-1,2-phenylenediamine.
† The transition could not be detected in cooling cycle.

temperature with stirring for over 1 h. The resulting yellow precipitate was filtered and washed with H_2O 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 65%. ^1H NMR (90 MHZ, $CDCl_3$) δ 11.52 (s, H^8, 1H), 10.18 (s, H^9, 1H), 8.26 (dd, H^2, 1H), 8.32 (d, H^3, 1H), 7.93 (d, $H^{4,7}$, 2H), 7.47 (d, $H^{5,6}$, 2H), 7.23(d, H^1, 1H), 2.70(t, H^A, 2H), 1.1–1.8(m, H^B, 20H), 0.91(s, H^C, 3H).

Synthesis of N,N′-bis-[2-hydroxy-5-(4′-n-dodecyl)phenylazobenzylidene]-1,2-dicyanoethylene diamine (5)

An ethanolic solution (20 ml) of 2-hydroxy-5-(4′-n-dodecyl)phenylazobenzaldehyde (0.79 g, 0.002 mol) was added to an ethanolic solution of diaminomaleo-nitrile (0.11 g, 0.001 mol). 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-dodecyl)phenylazobenzylidene]-1,2-dicyanoethylenediamine (5). The precipitate was collected by filtration and recrystallized from absolute ethanol. The overall yield varied between 60 ~ 70%. ^{1}H NMR (300 MHZ, $CDCl_3$) δ 11.30 (s, H^8, 1H), 10.03 (s, H^9, 1H), 8.17 (dd, H^2, 1H), 8.15 (d, H^3, 1H), 7.82 (dd, $H^{4,7}$, 2H), 7.32 (dd, $H^{5,6}$, 2H), 7.12(d, H^1, 1H), 2.65(t, H^A, 2H)1.18–1.68(m, H^B, 20H), 0.88 (s, H^C, 3H). Elemental analysis estimated C, 75.3; H, 7.96; N, 13.01.; Found C, 75.2; H, 7.89; N, 12.9.

All the analogous compounds **6–8** derived from 1,1-diamine viz., urea, 1,2-diamine viz., 1,2-phenylenediamine, and 1,3-diamine viz., 4-nitro-1,3-phenylenediamine were prepared as described for compound **5**. The elemental analysis and spectroscopic data gave satisfactory results.

RESULTS AND DISCUSSION

The sample **5** on heating has shown a transient ordered focal conic fan texture characteristic of the smectic phase but immediately transformed into a texture shown in Figure 1, indicating a transition to a thermodynamically more stable form. The mesophases, produced by slow cooling

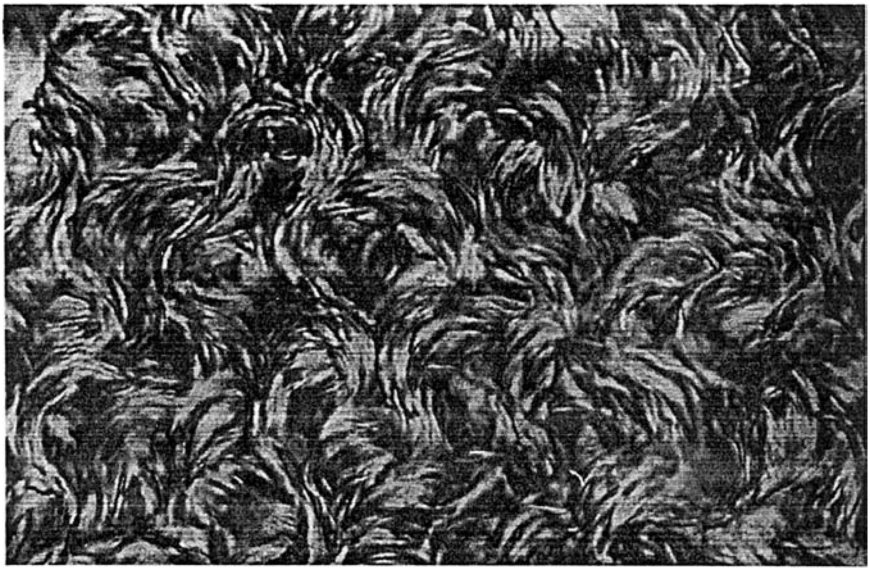


FIGURE 1 Optical photomicrograph (crossed polarizers) of the striated fan texture of the fluid smectic phase of the Compound **5** at 87°C.

of the isotropic phase of the sample, when observed by microscopy under polarizing light exhibited a striated arc or fanlike texture with homeotropic regions and showed that areas of uniform extinction dominate the texture as shown in Figure 1. The texture resembles the grainy texture of the B_2 phase reported in bent core mesogens [12]. This observation indicates that they have a strong tendency to orient their optical axis perpendicular to the substrate, i.e., the surface of the untreated glass microscopic slide. Further contact preparations showed the lack of miscibility of the liquid crystalline phase with the conventional smectic phases of nO.m compounds when viewed under microscope. The mesomorphic-isotropic transition enthalpy, which is considerably larger than the nematic or smectic-isotropic transition enthalpy, which is considerably larger than the nematic or smectic-isotropic transition, indicates a strong disruption of ordered structure.

It was reported [1] earlier that the degree of charge transfer in the ground state of molecules, possessing specific functional groups like nitrile groups, can be determined from the infrared absorption frequency of the CN stretch mode when the nitrile group is involved in a molecular system containing donor counterpart. In compound **5**, the observation that a bridging group possessing nitrile groups joins the wings with electron-donating ability and the observed frequency for CN stretch mode at $2210\,\mathrm{cm}^{-1}$ strongly suggests such hypothesis. However, further work is in progress for the establishment of charge transfer characteristics of this compound and its complexes with Cu(II), Co(II), and Ni(II).

Following the success of the material exhibiting liquid crystalline behavior, we experimented with a few other bridging groups viz., urea, 1,2 phenylene diamine, and 1,3 phenylene diamine which can promote the longitudinal polarizability to synthesize polar mesogens. All the samples are found to be mesomorphic and yet to be characterized for their liquid crystalline phases. The different bridging groups in the compounds **5**–**8** allow the conjugation, thereby promoting the augmentation of molecular polarizability. The phase transition temperatures and the associated transition enthalpies of the compounds **5**–**8** are presented in Table I and all the compounds exhibited moderately low melting points, which is a desirable attribute for this class of correlated mesophases manifested by a strong transverse dipole moment. Such strong dipolar forces may cause the molecules to display a time-averaged antiparallel organization of nearest neighbors. Moreover, all themolecules are clearly noncentrosymmetric. A permanent dipole moment can be expected along the twofold symmetry axis as a result of the electronic donor-π-acceptor system in each wing, and hence nonvanishing components along the length of the two azo wings are manifested. In the molecules with the bent rod shape that possess a strong transverse dipole moment, a highly dipolar nature produces strong orientational correlations between nearest neighbors [13]. These molecular structures with large hyperpolarizability and nonlinear optical coefficients should be well suited for further studies. The physical studies are in progress to characterize and explore the importance of these materials.

CONCLUSION

We have synthesized a series of a banana or V-shaped molecules derived from 2-hydroxy-5-(4′-n-dodecyl)phenylazobenzaldehyde which can act as electron donor condensing with differing bridging groups possessing electron with drawing groups to act as charge transfer molecule with bent shape imposed by molecular structure. All the materials exhibit liquid crystalline behavior at ambient temperatures, which can be coordinated with metals for possible exploration for their utility as nonlinear optical materials. The optical textures indicate ordered molecular ordering that does not match the conventional calamitic liquid crystalline textures. However, to understand the molecular structures we need to collect more experimental data on optical switching phenomena and hyperpolarizability data on these achiral systems. The photoisomerization characteristics of such materials are yet to be studied for possible photophysical applications.

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