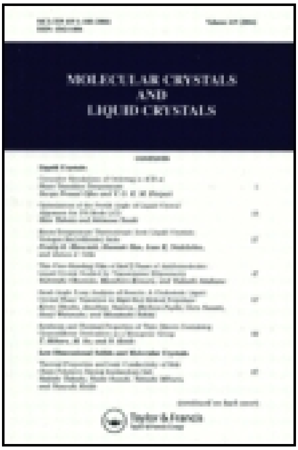

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Novel Liquid-Crystalline Mercury Acetylide Complexes

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Novel Liquid-Crystalline Mercury Acetylide Complexes

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Several new mercury acetylide complexes were prepared from substituted phenyl acetylenes. These are of three varieties: i) where normal or branched alkyl chains are attached to the phenyl ring directly, ii) where these chains are attached via an oxygen atom (alkoxy chains), and iii) where the phenyl ring is substituted by two or three alkoxy chains. All the alkoxy derivatives are liquid crystalline. Their mesomorphism has been examined by polarizing microscopy and differential scanning calorimetry.

Keywords: Metallomesogens; mercury acetylides; organomercury complexes; liquid crystals

INTRODUCTION

Liquid crystals incorporating metals (now commonly known as metallomesogens) have received a considerable interest in the last 20 years and a large number of metallomesogens have been synthesized. The chemistry and physics of metallomesogens have recently been covered in several review articles [1–4]. Formation of metal salt by acetylenes is known since more than a century [5]. The linear shape of these metal acetylides is suitable for the formation of liquid crystalline phases. The symmetrical linear mercury(II) derivatives where the mercury atom is covalently linked with two phenyl groups (Fig. 1) were described in 1923 [6]. These symmetrical as well as non symmetrical mercury complexes were reported to form smectic phases [3, 6]. Formation of smectic A mesophase was also observed in bis(p-n-hexyloxyphenyl)mercury [7]. Substituted biphenyls connected *via* mercury atom were reported by Chandrasekhar but

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their mesophases could not be characterized due to the unstable nature of these materials [8]. Synthesis and characterization of chiral smectic C^* mesophases of azoxymercury complexes has also been reported recently [9]. Normally organometallic compounds possessing a direct metal-carbon bond are considered to be chemically and thermally unstable, however, it is known that metal-alkynyl linkage is significantly more stable [3]. Several new series of liquid crystalline materials covalently linked with various metals such as palladium, platinum, gold, etc., have appeared in the literature [3, 10].

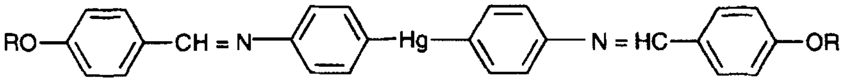


FIGURE 1

For the preparation of various discotic nematic liquid crystals based on hexa- and pentaalkynylbenzene, we have recently prepared various phenylacetylenes [11]. These phenylacetylenes were easily converted into mercury bridged dimers. Here we report on the synthesis and characterization of these novel mercury acetylides.

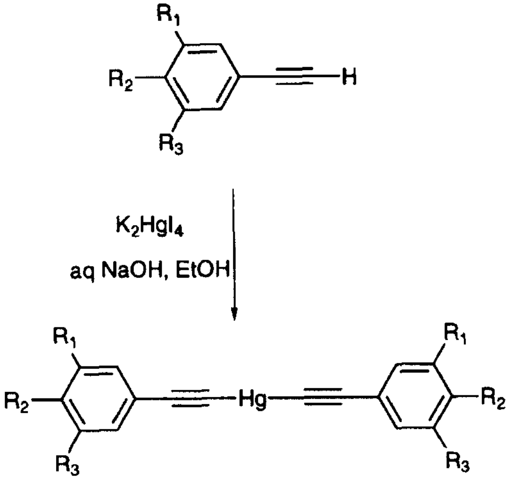
EXPERIMENTAL

General Information

Chemicals and solvents (AR quality) were used as such without any purification. Column chromatographic separations were performed on silica gel (70–230 and 200–400 mesh). Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). Mass spectra were recorded on a JEOL JMS-600H spectrometer in FAB+ mode using m-nitrobenzylalcohol (NBA) matrix. ^{1}H NMR spectra were recorded in $CDCl_3$ on a 200 MHz Bruker Aveance Series DPX-200 NMR spectrometer. All chemical shifts are reported in δ (ppm) units downfield from Me_4Si, and J values are given in Hz. IR spectra were recorded on a Perkin Elmer Spectrum 1000 spectrometer. Transition temperatures were measured using a Mettler FP82HT hot stage and central processor in conjunction with Leitz DMRXP polarizing microscope as well as by differential scanning calorimetry (DSC7 Perkin-Elmer).

Synthesis

Synthesis of different mercury acetylides outlined in the Scheme 1.



1a. $R_1 = R_3 = H$, $R_2 = -CH_2(CH_2)_8CH_3$

1b. $R_1 = R_3 = H$, $R_2 = -CH_2(CH_2)_{10}CH_3$

1c. $R_1 = R_3 = H$, $R_2 = -CH_2(CH_2)_2CH(CH_3)(CH_2)_4CH_3$

1d. $R_1 = R_3 = H$, $R_2 = -OCH_2(CH_2)_7CH_3$

1e. $R_1 = R_3 = H$, $R_2 = -OCH_2(CH_2)_8CH_3$

1f. $R_1 = R_3 = H$, $R_2 = -OCH_2(CH_2)_{10}CH_3$

1g. $R_1 = R_3 = H$, $R_2 = -OCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$

1h. $R_1 = H$, $R_3 = CH_3$,
$R_2 = -OCH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$

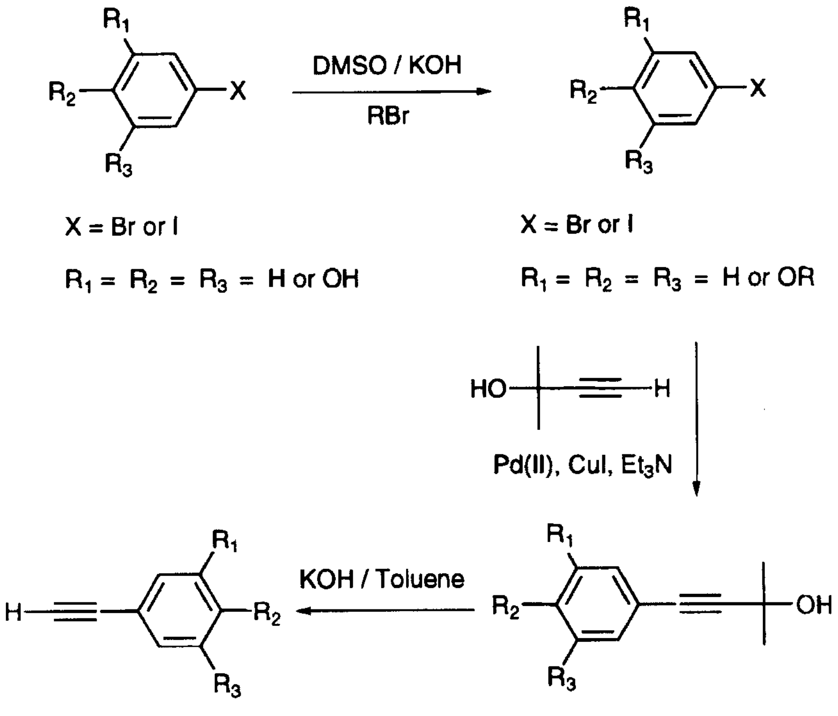
1i. $R_1 = H$, $R_2 = R_3 = -OCH_2(CH_2)_3CH_3$

1j. $R_1 = H$, $R_2 = R_3 = -OCH_2(CH_2)_{10}CH_3$

1k. $R_1 = R_2 = R_3 = -OCH_2(CH_2)_3CH_3$

SCHEME 1 Synthesis of various mercury acetylides

4-alkyl phenylacetylenes were prepared as reported [12]. All the alkoxy phenylacetylenes were prepared by standard methods shown in Scheme 2 which comprises alkylation of bromo- or iodophenols with various alkyl bromides, reacting the resultant alkoxybromobenzenes with 2-methyl-3-butyn-2-ol to yield the corresponding protected phenyacetylenes and finally deprotecting the protected phenylacetylenes to yield the corresponding phenylacetylenes. All the compounds were purified by column chromatography and characterized from their spectral analysis.



SCHEME 2 Synthetic route for the preparation of various alkoxyphenylacetylenes

Synthesis of bis-(phenylethynyl)mercury complexes

The mercury complexes were prepared following the literature proceedure [13]. Into a cooled, freshly prepared dilute solution of alkaline mercuric iodide (about 2 equivalent) was added drop-wise a solution of phenylacetylenes (1 equivalent) in a mixture of ethanol and ether. The light yellow precipitate or gummy solid was filtered and washed with water. It was taken in ether and recrystallized from hexane-ether.

Bis-(4-n-decyl phenylethynyl)mercury, 1a

MS: m/z: 684.5, IR (KBr): 2957, 2920, 2851, 2145, 1508, 1468, 1425, 1375, 1219, 1024; ^{1}H NMR: δ 7.39 (4H, d, J = 8.0), 7.13 (4H, d, J = 8.0), 2.60 (4H, t, J = 7.8), 1.57 (4H, br s merged with H_2O signal), 1.25 (28H, br s), 0.88 (6H, t, J = 6.9).

Bis-(4-n-dodecyl phenylethynyl)mercury, 1b

MS: m/z: 738.9; ^{1}H NMR: δ 7.39 (4H, d, J = 8.1), 7.12 (4H, d, J = 8.1), 2.60 (4H, t, J = 7.6), 1.57 (4H, br s), 1.25 (36H, br s), 0.88 (6H, t, J = 6.6).

Bis-(4-(4-methylnonanyl phenylethynyl)mercury, 1c

MS: m/z: 684.4; ^{1}H NMR: δ 7.39 (4H, d, J = 8.1), 7.12 (4H, d, J = 8.1), 2.58 (4H, t), 1.6–1.1 (26H, m), 0.87 (12H, m).

Bis-(4-n-nonanyloxy phenylethynyl)mercury, 1d

MS: m/z: 688.0; ^{1}H NMR: δ 7.41 (4H, d, J = 8.8), 6.83 (4H, d, J = 8.8), 3.95 (4H, t, J = 6.5), 1.76 (4H, m), 1.6–1.2 (24H, m), 0.88 (6H, t, J = 6.7).

Bis-(4-n-decyloxy phenylethynyl)mercury, 1e

MS: m/z: 714.9; ^{1}H NMR: δ 7.41 (4H, d, J = 8.8), 6.83 (4H, d, J = 8.8), 3.95 (4H, t, J = 6.5), 1.77 (4H, m), 1.6–1.2 (28H, m), 0.88 (6H, t, J = 6.7).

Bis-(4-n-dodecyloxy phenylethynyl)mercury, 1f

MS: m/z: 770.6; ^{1}H NMR: δ 7.41 (4H, d, J = 8.8), 6.83 (4H, d, J = 8.8), 3.95 (4H, t, J = 6.5), 1.75 (4H, m), 1.6–1.2 (32H, m), 0.88 (6H, t, J = 6.7).

Bis-(4-(3,7-dimethyl)octyloxy phenylethynyl)mercury, 1g

MS: m/z: 716.3; ^{1}H NMR: δ 7.40 (4H, d, J = 8.8), 6.82 (4H, d, J = 8.8), 3.99 (4H, t, J = 6.5), 1.8–1.0 (20H, m), 0.94 (6H, d, J = 6.5), 0.87 (12H, d, J = 6.5).

Bis-(3-methyl-4-(3,7-dimethyl)octyloxy phenylethynyl)mercury, 1h

MS: m/z: 742.7; ^{1}H NMR: δ 7.31–7.26 (4H, m), 6.74 (2H, d, J = 8.1), 4.03 (4H, t, J = 6.6), 2.18 (6H, s), 1.9–1.0 (20H, m), 1.0–0.80 (18H, m).

Bis-(3, 4-di-n-pentyloxy phenylethynyl)mercury, 1i

MS: m/z: 747.0; ^{1}H NMR: δ 7.05 (2H, dd), 6.99 (2H, d), 6.79 (2H, d), 3.99 (8H, m), 1.78 (8H, m), 1.6–1.2 (16H, m), 0.93 (12H, t).

Bis-(3, 4-di-n-dodecyloxy phenylethynyl)mercury, 1j

MS: m/z: 1138.3; ^{1}H NMR: δ 7.05 (2H, dd), 6.98 (2H, d), 6.79 (2H, d), 3.99 (8H, m), 1.78 (8H, m), 1.6–1.2 (72H, m), 0.88 (12H, t).

Bis-(3, 4, 5-tri-n- pentyloxy phenylethynyl)mercury, 1k

MS: m/z: 918.3; ^{1}H NMR: δ 6.68 (4H, s), 3.96 (12H, m), 1.8 (12H, m), 1.7–1.2 (24H, m), 0.92 (18H, t).

RESULTS AND DISCUSSION

The formation of mercury salts from substituted acetylenes is well known in the literature and this property may be utilized for the identification and characterization of the corresponding acetylenes [13]. Linear substituted acetylides of gold, platinum, mercury, etc., have recently been reported to form smectic and nematic phases [10, 14]. To further explore metal acetylides for their liquid crystalline properties, we prepared several new mercury acetylide complexes. These are of three varieties: i) where normal or branched alkyl chains are attached to the phenyl ring directly, ii) where these chains are attached via oxygen atom (alkoxy chains), and iii) where the phenyl ring is substituted by two or three alkoxy chains. The thermal data (phase transition temperatures) of all the compounds **1a-1k** are collected in Table I. Peak temperatures obtained in the heating and cooling DSC run are given in °C.

TABLE I Phase transition temperatures (peak temperatures) of mercury complexes **1a-k**. Cr = crystal, Sm$^+$ = believed to be smectic C, see the text for details, Col = columnar liquid crystalline phase, I = isotropic, LC = unidentified mesophase

Compound	*Thermal transitions (°C)*	
	Heating scan	*Cooling scan*
1a	Cr 99.4 I	I 96.1 Cr
1b	Cr 102.3 I	I 99.0 Cr
1c	Cr 100.0 I	I 98.0 Cr
1d	Cr 62.4 Sm$^+$ 120.7 I	I 118.1 Sm$^+$ 49.6 Cr
1e	Cr 68.6 Sm$^+$ 124.8 I	I 123.9 Sm$^+$ 62.3 Cr
1f	Cr 58.8 Cr 74.5 Sm$^+$ 126.2 I	I 122.5 Sm$^+$ 62.9 Cr
1g	LC 77.5 I	I 65.7 LC
1h	Col 57.1 I	I 52.1 Col
1i	Cr 72.9 Col 125.4 I	I 123.1 Col
1j	Cr 23.0 Cr 53.7 Col 106.3 I	I 104.3 Col 14.0 Cr
1k	Cr 66.9 LC121.7 I	I 119.5 LC

All the compounds in which aliphatic chains are attached to the phenyl ring via an oxygen atom are mesomorphic. The three compounds **1d, 1e** and **1f** having a normal alkoxy chains show an enantiotropic mesophase. On cooling from the isotropic phase, the samples exhibit either a broken focal conic texture or more often a schlieren texture. Figures 2a-2c show texture photograph of the mesophase shown by compounds **1d**, **1e** and **1f** respectively. Whenever the schlieren texture appeared it showed the following features: (a) No two brush disclination [s = 1/2, s being the strength of the disclination]. (b) A few four brushes (s = 1) meeting points and (c) a large number of points at which more than four brushes meet. The absence of two brush disclinations together with the appearance of broken focal conic texture rules out the possibility of the mesophase being a nematic phase. But the existence of "high strength defects", where more than four brushes meet needs a little more consideration. It may be recalled that high strength defects have been reported for the nematic phase in a few instances [15–18] and for the chiral smectic C phase in one case [19]. As the nematic phase is ruled out for the present case, we tentatively believe that the mesophase may be of the smectic C type. Lower homologues of this series have recently been reported to form nematic and SmA phases [14]. Formation of nematic phases at short chain length and smectic phases with longer chain length is common in calamitic liquid crystals [20].

The use of branched chains to modify the thermal properties, often to reduce the melting point, has been well documented [21]. In the present series, when the normal alkyl chain is replaced by a branched chain, compound **1g** precipitated out in the liquid crystalline phase from the etheral solution upon the addition of ethyl alcohol. On heating, it transforms to the isotropic phase at 77.5°C but upon cooling it does not show any defined optical texture between crossed polarizer and stayed in the optically isotropic form. When the cover glass on the sample was pressed, it showed some flow induced birefringence, but recovered the optical isotropic nature on release of pressure on the glass. Therefore, it is difficult to assign the nature of this mesophase. This compound also does not crystallize upon cooling down to –60°C (the lowest temperature to which the sample was cooled to). A lateral methyl branched substitution in this molecule (compound **1h**) reduces, as expected, the isotropic temperature and the compound shows mosaic textures upon cooling the isotropic phase. These textures resemble well with the typical textures of columnar mesophases (see Fig. 3a). When the number of alkoxy chains are increased from one to two in the precursor molecule, the dimer **1i** and **1j** leads to mercury complexes showing columnar organization. Compound **1i** melts at 72 °C and clears at 123 °C, while compound **1j** melts at 53.7 °C and clears at about 106 °C. Upon cooling from the isotropic phase, both the compounds show textures closely resembling the known textures

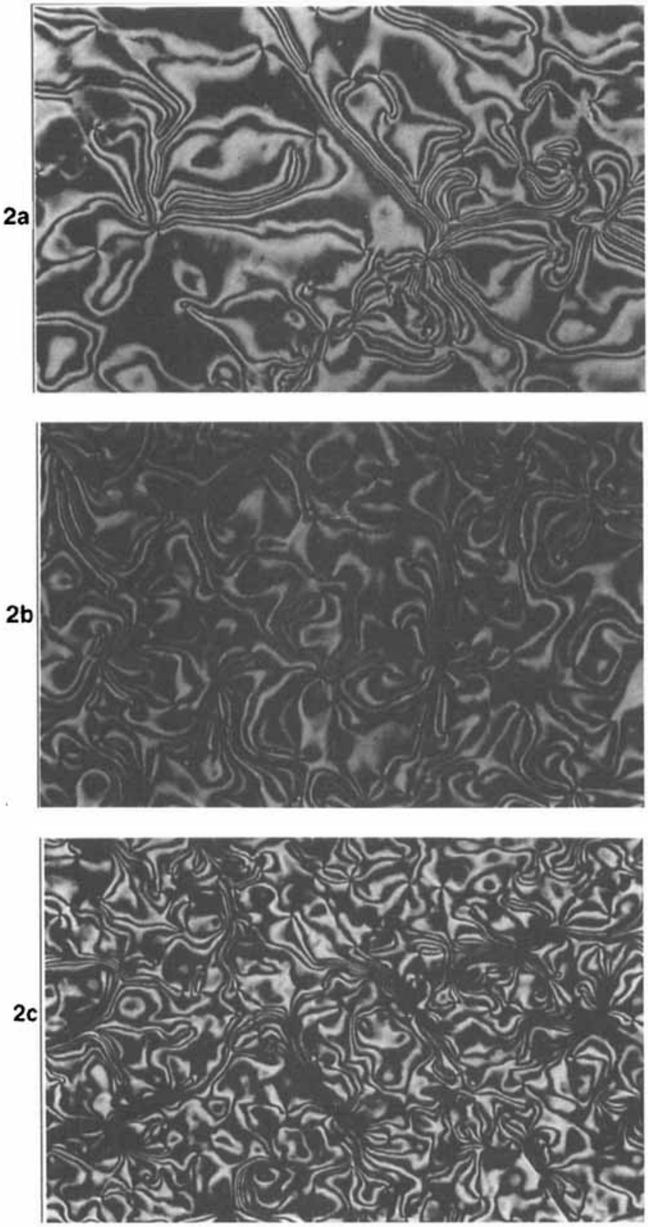


FIGURE 2A-C Disclination defect shown by the mesophase (believed to be smectic C phase, see text for details) of compounds **1d** (at 115°C), **1e** (at 90°C) and **1f** (at 120°C) respectively (crossed polarizer, magnification × 320). High strength defect observed here are quite rare (See Color Plate I at the back of this issue)

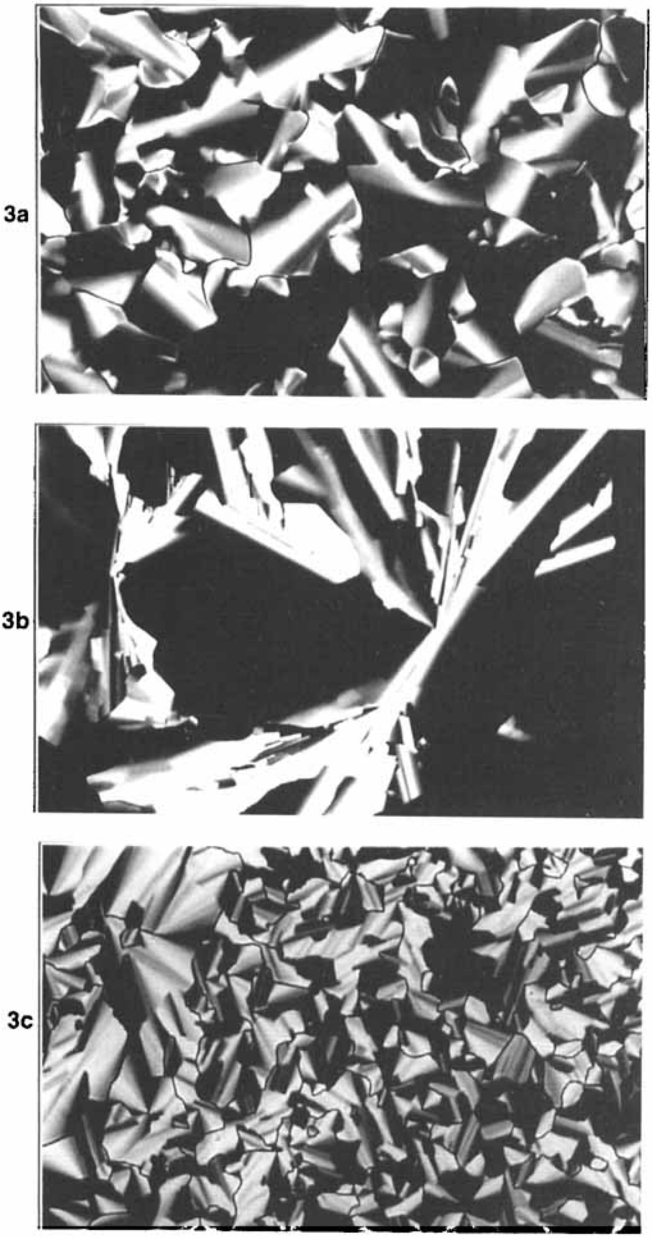


FIGURE 3A-C Mosaic pattern shown by compound **1h** (at 54°C), **1i** (at 122°C) and **1j** (at 61°C) respectively (crossed polarizer, magnification × 320). These textures resemble the usual textures of columnar phase shown by disc-like molecules (See Color Plate II at the back of this issue) for columnar phase (see Fig. 3b and 3c). While compound **1j** crystallizes at 14.0 °C and the melting and clearing transitions are reversible, compound **1i** does not show any sign of crystallization upon cooling down to −60°C and on second heating it shows only mesophase to isotropic transition at 124°C. The formation of columnar phases in these type of molecules due to the dimer formation is well documented [22]. When the number of alkoxy chains are increased to three in the precursor molecule, the metal complex **1k** shows the melting transition at 66.9°C and clearing transition at 121.7 °C. Upon cooling, the isotropic to mesophase transition occurs at 119.5 °C but like **1g**, this compound also does not show any definite texture, stay optically isotropic and the nature of the mesophase could not be ascertained.

All the three compounds in which the alkyl chain is directly connected to the phenyl ring, are non mesogenic. It is well known that linking group between the core and aliphatic chain has marked effects on liquid crystalline properties of the molecule. It is evident from the literature that when the peripheral alkyl chains in liquid crystalline compounds are attached to the phenyl ring *via* a hetero atom such as an oxygen atom, the melting and clearing temperatures are higher compared to when the alkyl chains are directly attached to the ring [23, 24]. While such a conformation can beneficially be utilized to reduce the melting point in some discotic liquid crystals [11], in the present calamitic case, liquid crystallinity is completely lost probably due to the loss of planarity of the molecule. This loss of mesogenicity underscores the significant influence of molecular conformation on the delicate balance between crystallization and mesophase formation.

It should be noted that the assignment of all the mesophases was determined only by polarized optical microscopy. Our efforts to confirm these phases by X-ray studies met with failure as all the compounds absorb x-ray strongly and any precise information from x-ray diffraction studies could not be obtained.

CONCLUSION

We have prepared several new mercury acetylide complexes showing stable smectic and columnar mesophases. These materials may be interesting for various physical studies.

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