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Synthesis, Characterization and Mesomorphic Properties of n-(4-n-Alkoxy-2-Hydroxybenzylidene)-4-Carbethoxyaniline and their Copper Complexes

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SYNTHESIS, CHARACTERIZATION AND MESOMORPHIC PROPERTIES OF n-(4-n-ALKOXY-2-HYDROXYBENZYLIDENE)-4-CARBETHOXYANILINE AND THEIR COPPER COMPLEXES

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New homologous series of N-(4-n-alkoxy-2-hydroxybenzylidene)-4-carbethoxy-aniline, $H_{2n+1}C_nOC_6H_3(OH)C(H)=NC_6H_4COOC_2H_5$ ($n = 6, 8, 10, 12, 16$) have been synthesized. These compounds were reacted with copper acetate to get the metal complexes. All these compounds have been characterized by elemental analysis, FT-IR and NMR spectroscopy. Mesomorphic properties of these compounds were studied by differential scanning calorimeter and polarizing microscope. These compounds exhibit wide range enantiotropic SmA phase as confirmed by their typical optical texture under polarizing microscope. In the heating cycle, all the members of the series (hexyl to hexadecyl) show SmA phase in the range of 70 to 115°C and this range is almost independent of the alkoxy chain (except in decyl). All the members show supercooling effect and the range of SmA phase is increased in the cooling cycle in comparison to the corresponding heating cycle. The copper (II) complexes of the series also show enantiotropic SmA phase but at higher temperatures (above 140°C) with decreased temperature range of existence in comparison to organic compounds.

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INTRODUCTION

Metallomesogens (metal containing liquid crystals) is a promising area of research [1–5] in liquid crystals due to perceived advantages of combining the properties of transition metals (colour and magnetism) with those of liquid crystals. The incorporation of metal ions opens the door to a rich variety of new geometrical shapes, which are not obtainable in totally organic liquid crystals, and also results in interesting electrical, optical and magnetic properties.

The organic liquid crystalline species whose rigid core is salicylaldimine [6] have been found convenient starting materials for the preparation of metallomesogens. Copper (II) [7–29], nickel (II) [30–32], vanadyl (IV) [15,29,32–34] palladium (II) [35–37] and iron (III) [38–41] complexes of salicylideneamine derivatives have been reported to show liquid crystalline properties. The copper (II) complexes of salicylaldimine have been studied to establish structure-property relationship. In these efforts Hoshino *et al.* [20] have described the liquid crystalline properties of the complexes of the type bis [4-X-N-(4-Y-phenyl) salicylaldiminato] copper (II), with X = 4-alkoxybenzoyloxy and Y = ethoxy (three ring ligand type) exhibiting nematics and/or smectic C (SmC) phases. When the whole N-(4-Y-phenyl) moiety was replaced by the N-n-propyl group, the smectic phase was totally suppressed in the resulting complexes of N-alkyl two-ring ligands [21]. It has, further, been modified by removing benzoyloxy moiety from group X; these complexes of N-phenyl derivatives (two-ring ligand system) are smectogenic [22]. In 1984 Ovchinnikov and coworkers [42] were the first to design the complexes with X = Y = alkoxy (Fig. 1) and studied

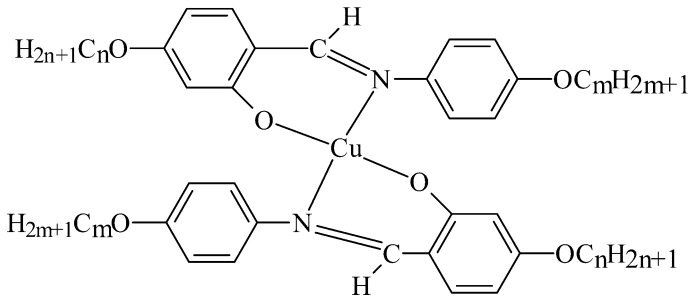


FIGURE 1 Molecular geometry of the Cu-complexes of salicylaldimine.

their mesogenic properties and reported them to be smectogenic. Since then either four long alkoxy [26,27,43,44] chains or two alkoxy (=X) and two alkyl (=Y) chains [8–11] have been employed. The molecular shape of these complexes is considered to be two roughly parallel rodlike moieties mutually head to tail oriented and connected by the metals. They are classified as lateral-lateral fused mesogens [45], the wider class of nondiscotic metallomesogens [1]. In such molecules the metallic core actually acts as a spacer between the two elongated frameworks. The present paper reports synthesis and mesomorphic properties of a series of new salicylaldimines and their copper (II) complexes. We have replaced Y by $CO_2C_2H_5$ (carbethoxy) group. It would be interesting as the polar nature of the corbonyl group plays a vital role in ferroelectric liquid crystals and this polarity can affect the mesomorphic and physicochemical properties of metal complexes in an unpredictable manner.

EXPERIMENTAL

H^1 NMR spectra ($CDCl_3$, TMS) have been recorded on a JEOL FX90Q spectrometer; the IR spectra (KBr pellets) have been carried out on a JASCO FTIR 5300 spectrophotometer. Transition temperatures and enthalpies have been determined with the help of differential scanning calorimeter (DSC) of Perkin-Elmer (model DSC-7) at the scanning rate of $10.0\,\text{K-min}^{-1}$. DSC has been calibrated at the scanning rate of $10.0\,\text{K-min}^{-1}$ using spec pure grade Zinc and Indium. The transition temperatures from DSC have been determined with the accuracy of ± 0.1 K. Uncertainty in the determination of transition enthalpies is less than 5%. The textures of the mesophases have been identified with the help of polarizing microscope of CENSICO (model Izumi-7626) fitted with a hot stage of Instec with temperature controlling accuracy 3 mK. Detail experimental techniques has already been discussed elsewhere [46].

SYNTHESIS OF THE LIGANDS

The synthesis of ligands has been carried out under a nitrogen atmosphere. The standard chemicals 2,4-dihydroxy benzaldehyde, ethyl 4-aminobenzoate (Aldrich), 1-bromoalkane (E-merck) and copper acetate (Aldrich) have been used as supplied.

Preparation of Ligand C_6LH

4-(n-Hexyloxy)-2-hydroxybenzaldehyde has been prepared by alkylating 2,4-dihydroxybenzaldehyde with RBr in EtOH/KOH described elsewhere

[8]. 4-(n-Hexyloxy)-2-hydroxybenzaldehyde (10 mmol) and ethyl 4-aminobenzoate (10 mmol) were mixed in ethanol (10 mL) and refluxed for 2 hours. The colour becomes yellow. The yellow precipitate that forms on cooling are filtered off and washed with ethanol and recrystallized from ethanol with the yield of 53%. All other homologous members of series have been prepared in a similar manner. Yield, NMR, IR and EA results for different members are summarized as follows.

C_6LH Yield 53%

H^1 NMR ($CDCl_3$, TMS), δ (ppm) 13.7 (s, 1H, OH), 8.7 (s, 1H, CH=N), 4.5 (q, 2H, CO_2CH_2), 4.0 (t, 2H, OCH_2), 0.9 (t, 3H, CH_3).

IR (KBr), ν (cm^{-1}) 2916, 2852 (CH_2), 1707 (COO), 1630 (C=N), 1591, 1510 (Ph), 1278, 1245 (OPh).

Elemental Analysis: Found (Calculated) C 71.65 (71.52), H 7.20 (7.36), N 3.75 (3.79).

C_8LH Yield 51%

H^1 NMR ($CDCl_3$, TMS), δ (ppm) 13.7 (s, 1H, OH), 8.7 (s, 1H, CH=N), 4.5 (q, 2H, CO_2CH_2), 4.1 (t, 2H, OCH_2), 0.9 (t, 3H, CH_3).

IR (KBr), ν (cm^{-1}) 2916, 2852 (CH_2), 1711 (COO), 1633 (C=N), 1593, 1510 (Ph), 1280, 1250 (OPh).

Elemental Analysis: Found (Calculated) C 72.50 (72.51), H 7.72 (7.86), N 3.58 (3.52).

C_{10}LH Yield 48%

H^1 NMR ($CDCl_3$, TMS), δ (ppm) 13.7 (s, 1H, OH), 8.7 (s, 1H, CH=N), 4.5 (q, 2H, CO_2CH_2), 4.1 (t, 2H, OCH_2), 0.9 (t, 3H, CH_3).

IR (KBr), ν (cm^{-1}) 2924, 2852 (CH_2), 1712 (COO), 1628 (C=N), 1595, 1511 (Ph), 1275, 1250 (OPh).

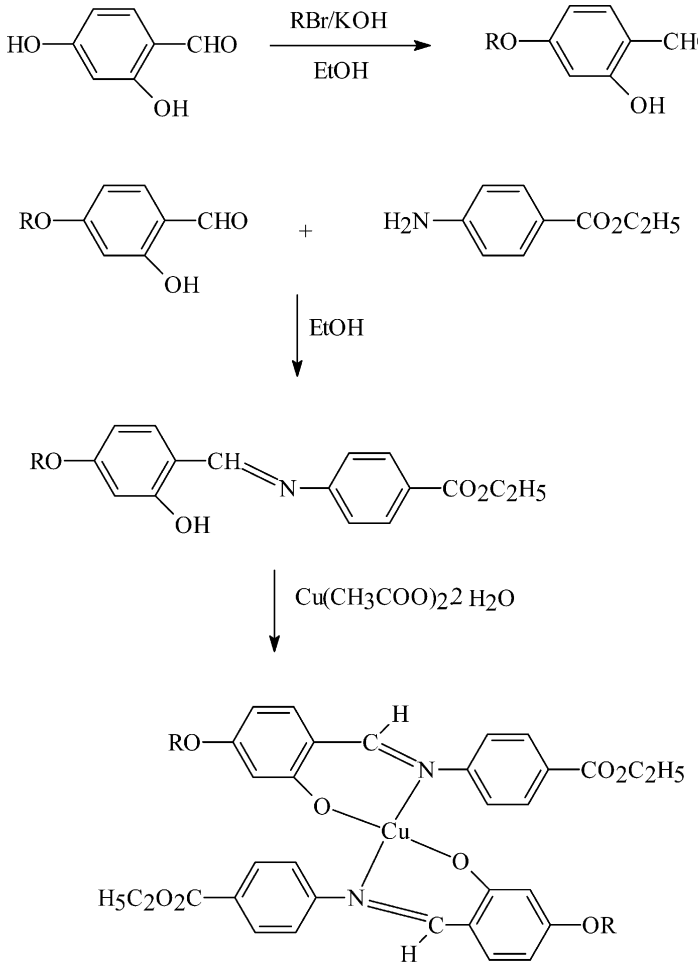
Elemental Analysis: Found (Calculated) C 73.50 (73.38), H 8.26 (8.29), N 3.34 (3.29).

C_{12}LH yield 49%

H^1 NMR ($CDCl_3$, TMS), δ (ppm) 13.7 (s, 1H, OH), 8.7 (s, 1H, CH=N), 4.5 (q, 2H, CO_2CH_2), 4.1 (t, 2H, OCH_2), 0.9 (t, 3H, CH_3).

IR (KBr), ν (cm^{-1}) 2924, 2852 (CH_2), 1712 (COO), 1628 (C=N), 1595, 1510 (Ph), 1275, 1249 (OPh).

Elemental Analysis: Found (Calculated) C 74.31 (74.14), H 8.82 (8.67), N 3.24 (3.09).



$R = C_6H_{13}, C_8H_{17}, C_{10}H_{21}, C_{12}H_{25}, C_{16}H_{33}$

SCHEME 1 Synthetic route for the ligands, C_nLH, and the corresponding copper (II) complexes.

$C_{16}LH$ Yield 43%

H^1 NMR ($CDCl_3$, TMS), δ (ppm) 13.7 (s, 1H, OH), 8.7 (s, 1H, CH=N), 4.5 (q, 2H, CO_2CH_2), 4.1 (t, 2H, OCH_2), 0.9 (t, 3H, CH_3).

IR (KBr), ν (cm^{-1}) 2924, 2852 (CH_2), 1712 (COO), 1628 (C=N), 1595,1512 (Ph), 1284, 1250 (OPh).

Elemental Analysis: Found (Calculated) C 75.50 (75.48), H 9.25 (9.29), N 2.72 (2.75).

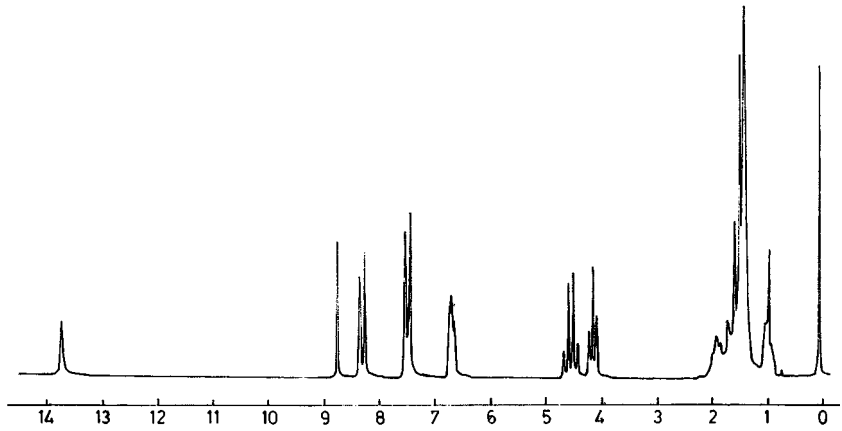
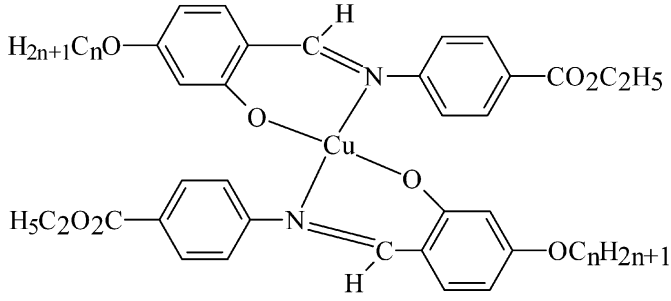


FIGURE 2 NMR spectrum of the ligand C_8LH.

SYNTHESIS OF COMPLEXES

Preparation of $(C_6L)_2Cu$

The copper complexes of C_6LH have been synthesized by adding copper acetate (99.82 mg, 0.5 mmol) in methanol to the solution of C_6LH (369.45 mg, 1 mmol) in methanol/chloroform (1/1, v/v, 20 ml). The mixtures have been stirred at room temperature for one hour. The resulting brown solid has been filtered off and washed with methanol. All the homologous members of series have been prepared in a similar manner. Yield, IR and EA results for different members are summarized as follows.



n = 6, 8, 10, 12, 16.

FIGURE 3 Molecular geometry of $(C_nL)_2Cu$.

TABLE 1 Transition Temperature (T), Transition Enthalpy (ΔH) and Transition Entropy (ΔS) of Ligands and their Copper Complexes

Compounds	Transitions	T/°C	ΔH/kJ-mol^{-1}	ΔS/J-mole^{-1}-K^{-1}
C_6LH	$K^1 \rightarrow K^2$	63.4	3.2	9.5
	$K^2 \rightarrow$SmA	70.8	27.7	80.5
	SmA→I	117.2	5.3	13.6
	I→SmA	113.0	5.0	12.8
	SmA→K	35.5	11.2	36.3
C_8LH	K→SmA	72.4	23.4	67.7
	SmA→I	118.1	3.7	9.5
	I→SmA	114.1	5.1	13.2
	SmA→K	25.1	8.5	28.5
C_{10}LH	K→SmA	86.7	41.2	114.5
	SmA→I	117.4	5.9	15.1
	I→SmA	114.5	5.5	14.2
	SmA→K	70.3	38.3	111.5
C_{12}LH	$K^1 \rightarrow K^2$	71.0	15.7	45.6
	$K^2 \rightarrow$SmA	73.5	33.1	95.5
	SmA→I	114.5	6.5	16.8
	I→SmA	112.7	6.1	15.8
	SmA→K	50.7	31.9	98.5
C_{16}LH	$K^1 \rightarrow K^2$	62.8	11.1	33.0
	$K^2 \rightarrow$I	82.8	48.0	135.0
	I→SmA	88.1	2.4	6.7
	SmA→K	63.7	38.2	113.4
Cu(C_6L)$_2$	K→I	197.4	45.5	96.7
	I→SmA	185.4	5.6	12.1
	SmA→K	154.5	31.3	73.2
Cu(C_8L)$_2$	$K^1 \rightarrow K^2$	102.1	3.5	9.2
	$K^2 \rightarrow$SmA	149.4	23.5	55.6
	SmA→I	178.7	9.4	20.8
	I→SmA	176.7	8.5	19.0
	SmA→K^2	116.3	21.9	56.1
	$K^2 \rightarrow K^1$	98.8	2.3	6.4
Cu(C_{10}L)$_2$	$K^1 \rightarrow$SmA	157.4	32.1	74.5
	SmA→I	183.4	10.3	22.6
	I→SmA	181.8	10.0	21.9
	SmA→K	121.3	27.9	70.8
Cu(C_{12}L)$_2$	$K^1 \rightarrow K^2$	117.3	24.9	63.7
	$K^2 \rightarrow K^3$	148.2	15.1	35.8
	$K^3 \rightarrow$I	215.7	51.8	106.0
	I→K^2	181.6	12.6	27.7
	$K^2 \rightarrow K^1$	165.6	18.1	41.3
Cu(C_{16}L)$_2$	$K^1 \rightarrow K^2$	70.6	70.4	204.8
	$K^2 \rightarrow K^3$	98.8	73.8	198.4
	$K^3 \rightarrow K^4$	112.7	24.7	64.0
	$K^4 \rightarrow$SmA	141.0	22.8	55.1
	SmA→I	165.5	9.2	21.0
	I→SmA	160.6	6.9	16.0
	SmA→K	105.2	42.1	111.2

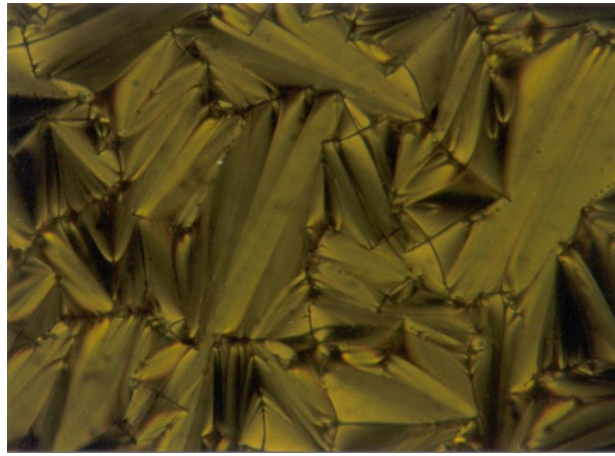


FIGURE 4 Optical texture of SmA phase in unaligned sample of the ligand $C_{10}LH$ (100X). (See COLOR PLATE I)

$(C_6L)_2Cu$ Yield 78%

IR (KBr), $\nu(cm^{-1})$ 2924, 2852 (CH_2), 1714 (COO), 1612 (C=N), 1593, 1510 (Ph), 1275, 1245 (OPh).

Elemental Analysis: Found (Calculated) C 66.15 (66.02), H 6.55 (6.54), N 3.45 (3.49).

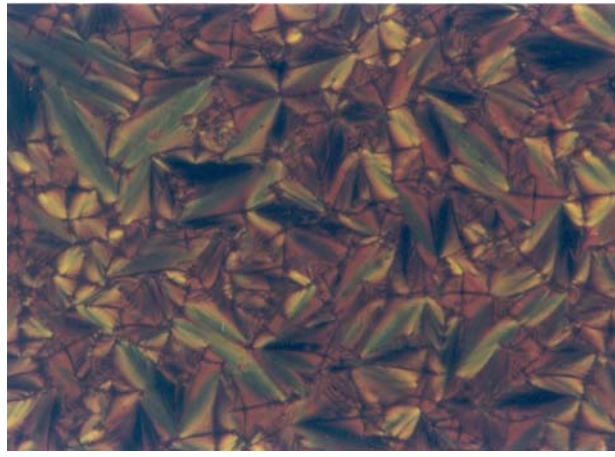


FIGURE 5 Optical texture of SmA phase in unaligned sample of the complex $(C_8L)_2Cu$ (100X). (See COLOR PLATE II)

$(C_8L)_2Cu$ Yield 75%.

IR (KBr), $\nu(cm^{-1})$ 2926, 2850 (CH_2), 1714 (COO), 1610 (C=N), 1580, 1510 (Ph), 1273,1250 (OPh).

Elemental Analysis: Found (Calculated) C 66.55 (67.31) H 7.11 (7.06), N 3.25 (3.27).

$(C_{10}L)_2Cu$ Yield 81%

IR (KBr), $\nu(cm^{-1})$ 2934, 2857 (CH_2), 1707 (COO), 1608 (C=N), 1585, 1511 (Ph), 1275, 1250 (OPh).

Elemental Analysis: Found (Calculated) C 68.50 (68.43), H 7.48 (7.51), N 3.02 (3.07).

$(C_{12}L)_2Cu$ Yield 72%

IR (KBr), $\nu(cm^{-1})$ 2922, 2852 (CH_2), 1709 (COO), 1608 (C=N), 1587, 1510 (Ph), 1277, 1249 (OPh).

Elemental Analysis: Found (Calculated) C 69.40 (69.42), H 7.94 (7.91), N 2.78 (2.89).

$(C_{16}L)_2Cu$ Yield 70%

IR (KBr), $\nu(cm^{-1})$ 2918, 2852 (CH_2), 1709 (COO), 1618 (C=N), 1593, 1512 (Ph), 1277, 1250 (OPh).

Elemental Analysis: Found (Calculated) C 71.05 (71.11), H 8.51 (8.58), N 2.63 (2.59).

RESULTS AND DISCUSSION

The ligands have been prepared in a two-step process as shown in the Scheme 1. The elemental analysis, IR and NMR spectra are fully consistent with the structure. The NMR spectrum of the C_8LH has been shown in Figure 2. Their copper complexes have been obtained by reacting the ligands C_nLH with $Cu(CH_3COO)_2.H_2O$ in 2:1 molar ratio, whose elemental analysis are in agreement with the expected stoichiometry of $(C_nL)_2Cu$. The IR spectra of the complexes have been compared with their parent ligands. The ν (C=N) is observed at lower frequency in complexes compared to that of the parent ligands. This indicates bonding of azomethine nitrogen to copper (II). The phenolic proton observed in the NMR spectra of the ligands disappears from the spectra of the complexes showing bonding of phenoxy oxygen to copper (II). All the metal complexes have been structurally characterized and the molecular geometry for all the compounds have been proposed as sketched in Figure 3.

All the homologous series of ligands (n = 6, 8, 10, 12, 16) exhibit mesomorphism. The phase transition temperatures and transition enthalpies determined with the help of differential scanning calorimeter and polarizing

optical microscope have been summarized in Table 1. Symbols of K, SmA and I have been used to denote crystalline, smectic A and isotropic liquid phases, respectively. C_n indicates the number of carbon atoms in terminal alkyl chains. All the ligands melt nearly at 70°C (except $C_{10}LH$) and the fluids display typical fan shape optical texture of SmA phase under a polarizing optical microscope. All these compounds exhibit a wide temperature range of SmA phase. In the cooling cycle all the homologous series exhibit supercooling effect and so the range of SmA phase is increased. The optical texture of $C_{10}LH$ has been shown in the Figure 4. This range of mesophase is almost independent of the number of carbon atoms in the alkoxy chains. The ligands are thus highly mesogenic, which should be advantageous for furnishing liquid crystalline behaviour to metal complexes.

The copper complexes of the series also exhibit SmA mesophase, but at higher temperature (above 140°C) in comparison to their ligands. Table 1 summarizes the thermodynamical results for ligands and their copper (II) complexes. The optical texture of the $(C_8L)_2Cu$ has been shown in the Figure 5. The complex $(C_6L)_2Cu$ is monotropic. On heating it undergoes directly to isotropic liquid at 197.4°C and on cooling gives SmA phase between 185.4°C and 154.5°C. The compound $(C_{12}L)_2Cu$ does not exhibit mesomorphism but show polymorphism in crystal phases. The complexes $(C_8L)_2Cu$, $(C_{10}L)_2Cu$ and $(C_{16}L)_2Cu$ exhibit SmA mesophase at above 141°C and also show polymorphism in the crystal phase as shown in the Table1. These compounds show super cooling effect.

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