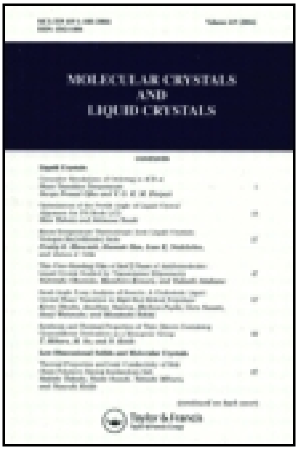

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New Chiral Polar Smectic C Liquid Crystals

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New Chiral Polar Smectic C Liquid Crystals†

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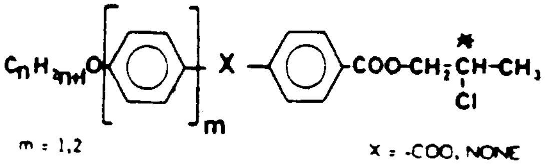
Applicability of ferroelectric liquid crystals to large screens handling high density information has been demonstrated. High speed and bistable effect are the greater advantages of these materials. The chemical problems to be solved were to synthesize broad-band room temperature substances with high polarisation, negative dielectric anisotropy, large pitch and adequate tilt angle.

A number of compounds having in their structure the R(-) 2 chloro propyl group have been synthesized.



The smectic stability for these series has been examined. Some compounds exhibit the chiral smectic C phase. All of them can be used as chiral dopants in broad-band room temperature mixtures. Some examples of these mixtures will be presented.

Keywords: liquid crystal, ferroelectric, smectic C, display, material, chiral

INTRODUCTION

The twisted nematic-type display mode is the most widely employed for liquid crystal display elements. Liquid crystal materials used in these electrooptical effects are mainly nematic or cholesteric liquid crystal materials, and because of their dielectric anisotropy ($\Delta\epsilon$), it is possible to align their long molecular axis in a given direction by

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†Presented at 11th International Liquid Crystal Conference, Berkeley, California, July 86.

an applied electric field. But the dielectric coupling force ($\Delta\epsilon.\vec{E}.\vec{E}$) is weak and the electrooptical response is too low and conventional twisted nematic liquid crystal displays are limited to about 64 ways multiplexing with acceptable angle of view. At present there are other alternative liquid crystal display technologies which may overcome these limitations. One uses ferroelectric smectic liquid crystals. Tilted, chiral smectic phases exhibit ferroelectricity.[1] This property, combined with the long range order of smectic phase was shown to exhibit very short switching times and memory (bistability).[2] Because of the helical structure of this material there is no polarisation. So, in order to produce a display effect, the helix must be unwound and it is achieved in the SSFLC mode[2,3] by a short distance between the electrodes ($\leq 2\ \mu m$).

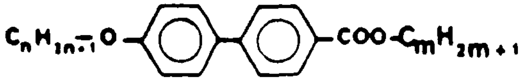
The technological problems associated with surface stabilised displays drove workers to induce bistability by other means.

A possibility is to use an A.C. stability effect.[4,5] In this operation, the bistability is given by the application of a high continuous frequency AC field sustaining the switching states in addition to the DC switching pulses. For this electrooptical effect, it is essential to have a negative dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} < 0$) chiral smectic C material for AC stabilisation and high polarisation to switch the state.

In this paper, we will present the synthesis and mesomorphic properties of new classes of liquid crystal materials containing chiral groups derived from S(-) ethyl lactate.

RESULTS AND DISCUSSION

It was found[6] for compounds of structure:



that these series of esters were characterised by an injection of S_c properties, usually at a carbon chain length of m = 4 and n = 7, 8, 9, which continued up to a chain length of n = m.

Various chiral smectic liquid crystal materials possessing this abovementioned chemical structure with a S(-) 3 methyl butyl group on the ester function have been synthesized and investigated.[7]

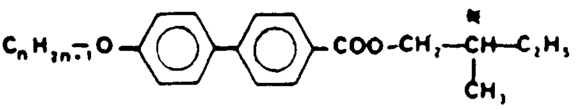


TABLE I

Mesomorphic properties of series (I)

n	Cr	S_c^*	S_A	I
6	.47,7	–	.66,4	.
7	.42,5	.43,2	.63,5	.
8	.46,1	(.43,7)	.63,5	.
9	.60,0	(.37,5)	.64,1	.
10	.49,9	(43,2)	.64,2	.

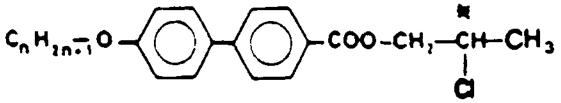
(T in °C)

( ) : monotropic transition
Cr : Crystal
S : Smectic
I : Isotropic

From the data given in Table I, it can be seen that the mesomorphism is unfortunately strongly monotropic but biphenyl ester type liquid crystal materials are noted for their chemical and photochemical stability and show a chiral smectic liquid crystal phase at temperatures relatively close to room temperature and they can be put into practical use in mixtures by adjusting a number of compounds.

Although the C* phase exists at low temperatures, the polarisation has a low value, so the switching speed is accordingly low.

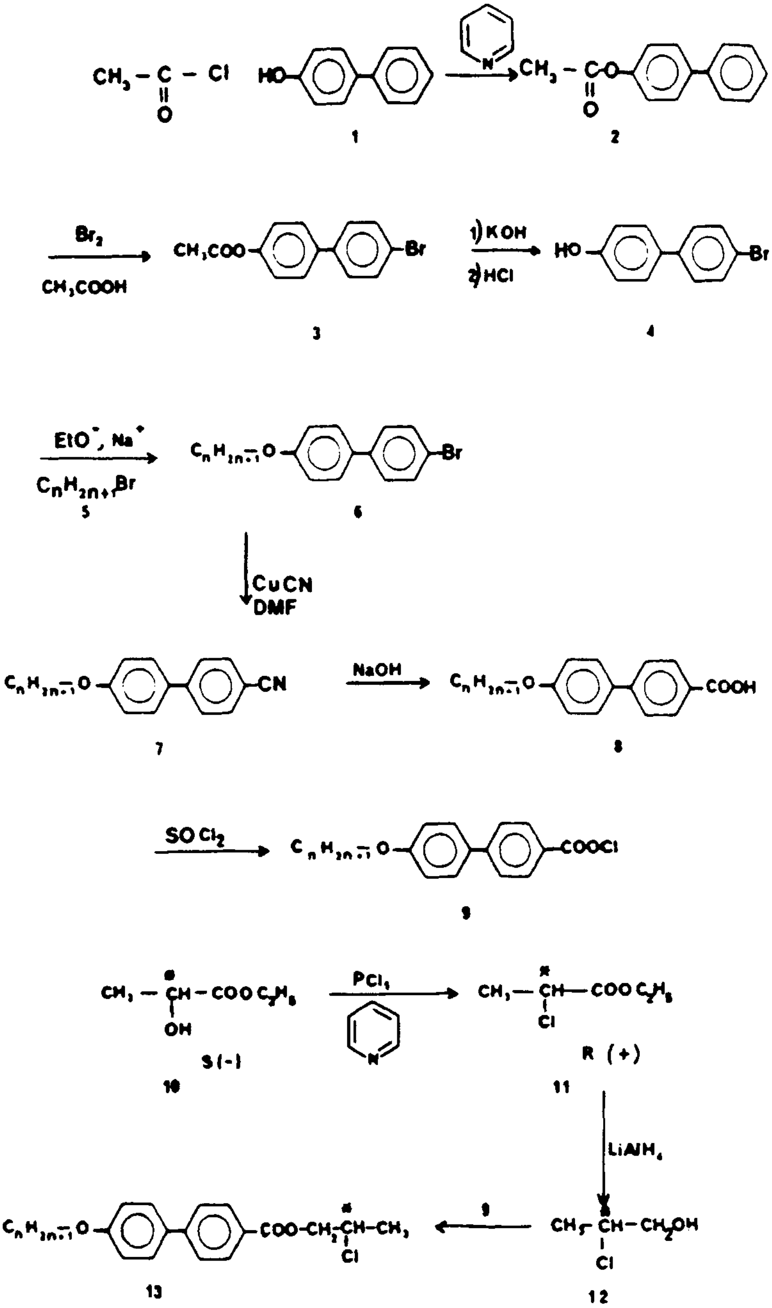
So, we have at first prepared some chiral liquid crystals by incorporation of the R(-) 2 chloro propyl group to have higher polarisation and lateral dipoles branched on the long molecular axis in order to obtain materials with negative dielectric anisotropy.



The synthetic route is given in Scheme 1.

The melting and transition points for the prepared compounds following the Scheme 1 are shown in Table II. Identifications of the mesophases have been done by examination of the textures (see experimental part) exhibited by thin samples sandwiched between two glass slides and by miscibility studies with reference compounds.

All the compounds prepared following the synthetic route of Scheme 1, give a smectic A phase. The behaviour of this series is very similar with those of esters given in Reference (6) and in Table I. Clearly, the replacement of (S) 3-methyl butyl group by the (R)-2 chloro


CH₃ – C – Cl
O
HO
1
N
CH₃ – C-O
O
2
Br₂
CH₃COOH
CH₃COO
Br
3
1) KOH
2) HCl
HO
Br
4
EtO⁻, Na⁺
CₙH₂ₙ₊₁Br
5
CₙH₂ₙ₊₁O
Br
6
CuCN
DMF
CₙH₂ₙ₊₁O
CN
7
NaOH
CₙH₂ₙ₊₁O
COOH
8
SOCl₂
CₙH₂ₙ₊₁O
COOCl
9
CH₃ – CH – COOC₂H₅
OH
S(-)
10
PCl₅
N
CH₃ – CH – COOC₂H₅
Cl
R (+)
11
LiAlH₄
CH₃ – CH – CH₂OH
Cl
12
9
CₙH₂ₙ₊₁O
COO-CH₂-CH-CH₃
Cl
13

SCHEME 1

TABLE II

Mesomorphic properties of series (II) compounds 13

Compound	n	Cr	S_A	I
13-5	5	.80 [5,84]	. 92,5 [2,26]	.
13-6	6	.62 [2,14]	.89 [1,03]	.
13-8	8	. 75 [5,73]	.86 [0,82]	.

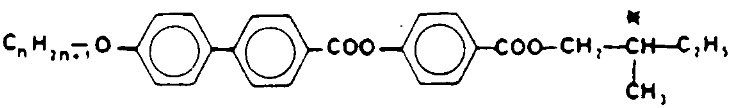
(T in °C)

( ) : monotropic transition
Cr : Crystal
S_A : Smectic A
[ ] : Enthalpy transition in Kcal/mole

propyl group has a dramatic effect on the chiral smectic C mesomorphism as shown by comparison of Table I and Table II. Incorporation of a bulky chloro group on the asymmetric carbon destroys completely the chiral smectic C mesomorphism and we can just notice a smectic A behaviour for this series (compounds 13). These materials can only be used as chiral dopants in mixtures to increase some parameters such as the polarisation. Presently investigated, chiral dopants can give more than $1 \mathrm{nCcm}^{-2}$ for every per cent of dopant introduced.

It can be expected that, if the valve of the distance between the liquid crystal core and the asymmetric carbon bearing a chloro group is greater, chiral smectic C behaviour will be injected with the advantage of increasing the pitch length. However, it has the disadvantage in reducing the strength of the polarisable nature of the material. In fact the nearer the chiral center is with the conjugated core system, the greater will be the strength of the ferroelectric dipole.

We have preferred to increase the length of the liquid crystal core in order to keep the same distance between the core system and the asymetric carbon. In fact, when we compare compounds of Table I with those of Table III, we can notice that all these compounds give an enantiotropic chiral smectic C phase.



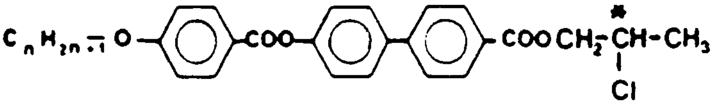
We report now some results on chiral liquid crystals having the same above-mentioned structure but with incorporation of (R)-2 chloro propyl group.

TABLE III

Mesomorphic properties of series (III)

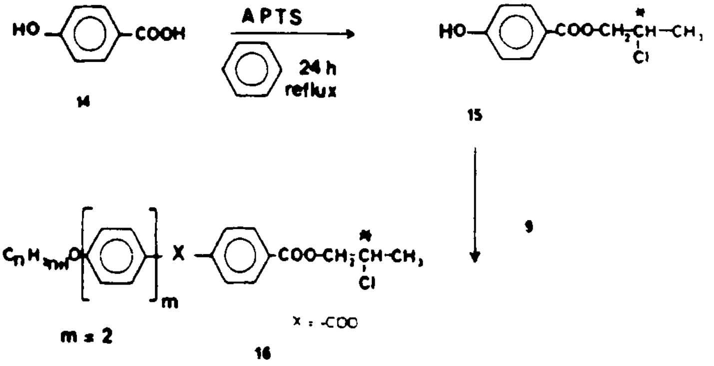
n	Cr	S_c^*	S_A	N*	I
7		.137	.192	-	.
8	.64	.139	.189	-	.

This has provided us with few compounds having the general structure (IV).



where n = 6 and 8.

The synthetic route is given in Scheme 2.



SCHEME 2

From the data given in Tables IVa, IVb, we can just notice the appearance of the chiral smectic C phase. Unfortunately, the mesomorphism is strongly monotropic and these compounds have very high melting and clearing points. It makes these compounds suitable for mixtures and for doping.

Eutectic mixtures

The temperature at which these ferroelectric phases exist are largely above room temperature and these phases are monotropic. For applications it is desirable to obtain the material in its ferroelectric phase at room temperature. The melting point of an eutectic mixture is

TABLE IVa

Mesomorphic properties of series (IV) compounds 16

Compound	n	Cr	S_3^*	S_c^*	S_A	I	
16-6	6	.68	(.79)	(.86)	.203	.	mp: 112
16-8	8	.58	-	(.72)	.194	.	mp: 104

(mp melting point)

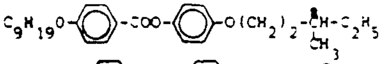
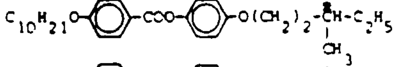
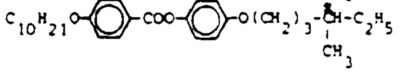
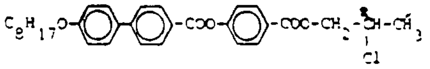
TABLE IVb

Enthalpy transitions for compounds 16 in cal/gram

Compound	Cr	S_3^*	S_c^*	S_A	I
16-6	. [12]	.[1,3]	.[0,79]	.[2,7]	.
16-8	.[11,8]	-	.[0,86]	.[2,9]	.

S_3^*: tilted ordered smectic not yet determined.

determined by application of the Schröder-Van Laar equation .[9] Furthermore, this technique produces mixtures with desired physical properties. Mixtures also provide the opportunity to control the pitch length of the phase by mixing materials of opposite twist sense given by the rule of Mac Donnell. A number of systems have been studied. The mixing of certain of these materials provide eutectic mixtures which exhibit C* phases at room temperature with the C* phase being succeeded by the A phase on heating. An example of these mixtures is given below.

		Helix
	32%	(S, even) Left handed
	26%	(S, even) Left handed
	42%	(S, odd) Right handed
	5%	(R, even) Left handed

Mixture of four compounds.

mp : 23°C

pitch ~ 10 μm

θ ~ *20° at 25°C*

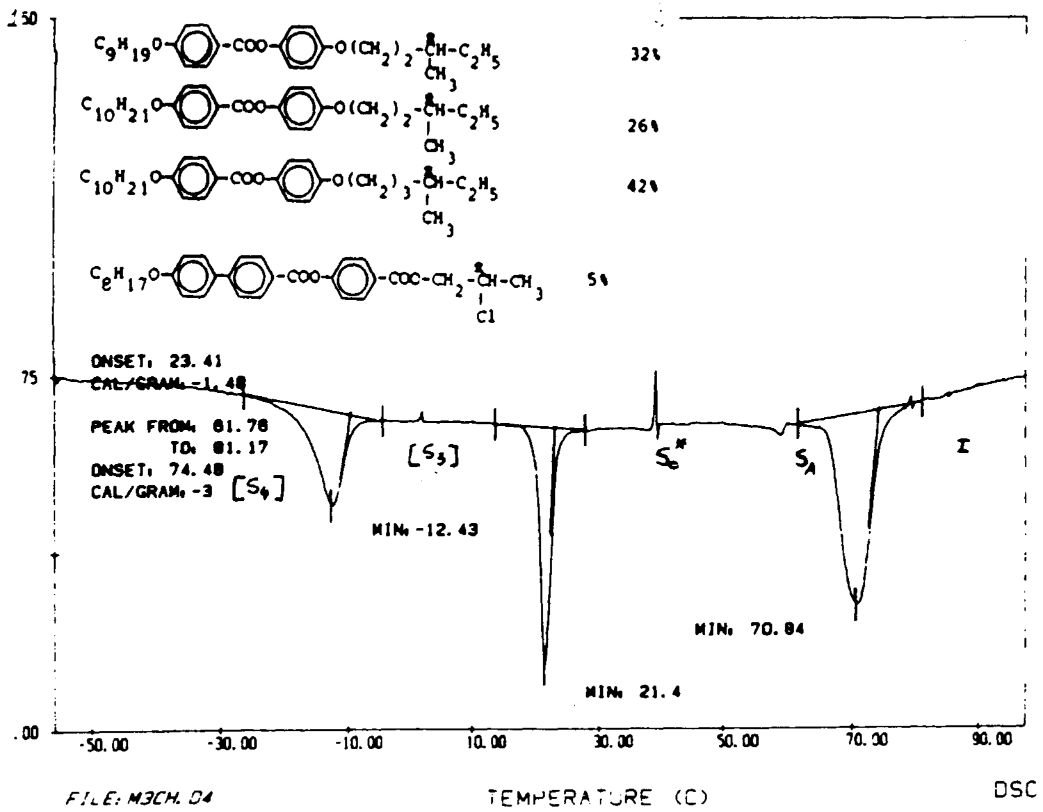


FIGURE 1 Differential scanning calorimetry measurement for the mixture of four compounds.

$\Delta\epsilon < 0$ not yet measured but negative because the molecules are sustaining under an A.C. field.

$$\rho \sim 3 \text{ n C cm}^{-2}$$

$$\eta \textit{ bulk} \sim \textit{120 cp.}$$

Conclusions

New polar families of chiral liquid crystals have been synthesized possessing in their structure the (R) 2 chloro propyl group. It has been found, that for a biphenyl core (structure (II)), all the compounds show only a smectic A phase and that for an increase of cores length (structure (IV)), it was possible to obtain monotropic chiral smectic C phase. However, all of them are suitable for broad-band room temperature mixtures as chiral dopants.

EXPERIMENTAL

Preparation of materials

All the esters above-mentioned were made by fairly standard procedures. The 4′-n-alkoxy biphenyl-4 carboxylic acids of structure 8 have already been prepared by Gray and Goodby (1980).[10]

The esters of structure 13 were prepared using an acid chloride method. To the carboxylic acid (8) (0,0015 mol), an excess of thionyl chloride (20 ml) was added and the mixture was heated under reflux for 3 hours. The hot solution was then evaporated to dryness and the resulting solid acid chloride was dissolved in pyridine (20 ml). This solution was cooled in ice and stirred. To this, a solution of the alcohol (12) in toluene was added. The mixture was allowed to stirr for 2 days. The solution was evaporated to dryness. The residue was taken in chloroform and the pure ester is obtained using a silica-gel column and chloroform as eluant. It was recrystallised from petroleum ether.

Preparation of compound (11). This compound was prepared by the interaction of (S) ethyl lactate (12 g) with phosphorus pentochloride (42 g) in pyridine (8 g) and the mixture was stirred during few hours. This solution was poured in ice, stirred and taken up in ether. The organic layer was washed several times with water, dried over anhydrous sodium sulphate. The ether solution was filtered and evaporated. The residue was then distilled under atmospheric pressure.

Preparation of (R) 2 chloro-propyl alcohol (12). The reduction is made with lithium-aluminum hydride in ether. The residue is distilled under reduced pressure (Teb 51°C under 30 mmHg).

Preparation of esters (16). The 4n hydroxy benzoïc acid and alcohol of structure (12) were dissolved in benzene. To this mixture was added toluene sulfonic acid (few ml). This mixture was heated under reflux (12 h with a Dean Stark). The benzene solution was filtered and evaporated. To this solution, petroleum-ether was added and the well-mixed solution was chilled in a refrigerator overnight. The resulting precipitate was filtered off and recrystallised from petroleum-ether, the hot solution again being filtered to remove any acid impurities.

Textures observed

The mesophase textures were observed using thin films of the samples (mounted between a glass slide and a cover slip) and a polarising microscope (Leitz orthoplan). The texture for smectic A phase of compounds 13 and 16 is the most common observed focal-conic fan texture. The phase separates out on cooling the isotropic phase in the form of batonnets. The batonnets, then coalesce and build up the focal-conic texture (see Figure 2). For compounds 16 on cooling,

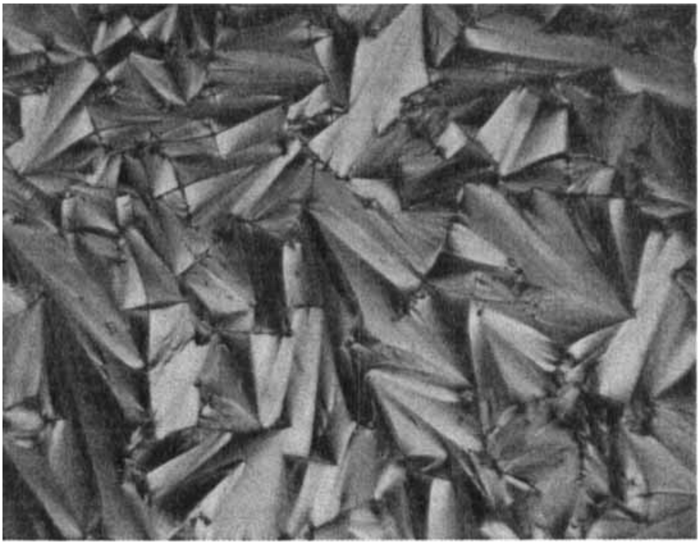


FIGURE 2 The focal-conic fan texture of the SmA phase compound 13-8. T = 81°C. (× 250). Color Plate I, see color plate section.

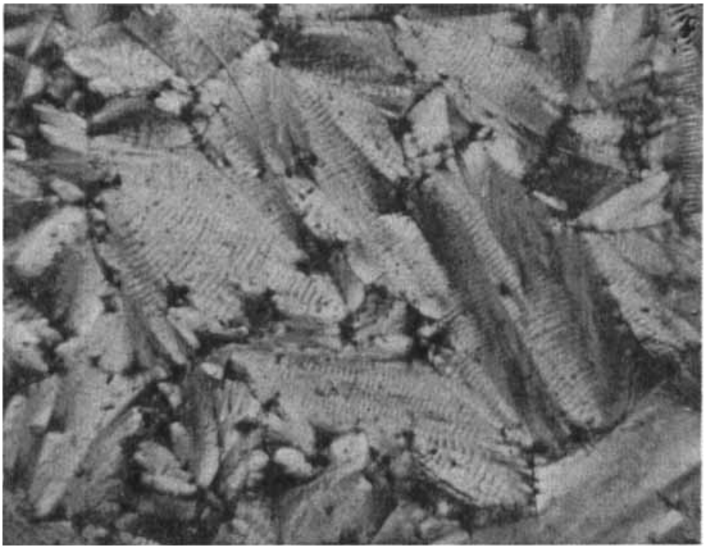


FIGURE 3 The banded focal-conic Fan texture of the chiral smectic C phase Compound 13-6. T = 75°C. (× 250). Color Plate II, see color plate section.

the fan texture of the A phase is broken giving the texture (see Figure 3) of the chiral smectic C phase (banded focal-conic fan texture).

Techniques

The melting points, transition temperatures, and enthalpies were determined using a Perkin-Elmer DSC 4 Differential Scanning Calorimeter.

The identification of intermediate products was carried out by the usual spectroscopic methods: IR (Perkin-Elmer 283), NMR (Brüker WP 80 CW).

Compounds were purified by using chromatography on silica gel column and their purity checked using the above-mentioned techniques.

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