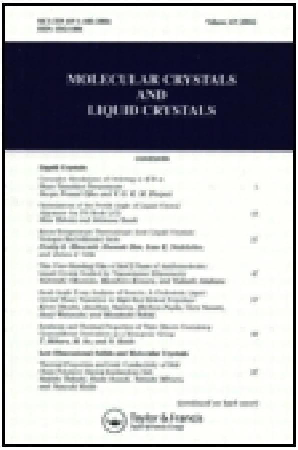

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Properties of Achiral and Chiral Esters with High Tilted Synclinic and Anticlinic Phases

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Version of record first published: 18 Oct 2010

To cite this article: J. Gasowska, R. Dabrowski, W. Drzewinski, K. Kenig, M. Tykarska & J. Przedmojski (2004): Synthesis and Mesomorphic Properties of Achiral and Chiral Esters with High Tilted Synclinic and Anticlinic Phases, Molecular Crystals and Liquid Crystals, 411:1, 231-241

To link to this article: http://dx.doi.org/10.1080/15421400490435224

Mol. Cryst. Liq. Cryst., Vol. 411, pp. 231/[1273]–241/[1283], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490435224

SYNTHESIS AND MESOMORPHIC PROPERTIES OF ACHIRAL AND CHIRAL ESTERS WITH HIGH TILTED SYNCLINIC AND ANTICLINIC PHASES

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Two series of three ring esters with chiral chain (derivative of (S)-octanol-2) and achiral chain (the swallow type) with high tilted synclinic and anticlinic phases were chosen to studies. The aim of presented studies was to find how the changes of different molecule units influence the mesomorphic properties of the compounds (temperatures, enthalpies and the sequence of phase transitions) and to find members with the best properties for mixture formulation. The compounds were studied by polarising microscope, differential scanning calorimetry, miscibility and X-ray diffraction methods.

Keywords: anticlinic and synclinic phase; antiferroelectrics; ferroelectrics; phase transition; synthesis

INTRODUCTION

During few recent years we have synthesized and investigated mesomorphic properties of three ring chiral esters having an perfluorinated unit in one terminal chain [1,2]. We have found that compounds with $C_sF_{2s+1}COO(CH_2)_3O$ tail have the smectic layer with anticlinic order and a very large tilt [3]. AFLC mixtures with the tilt 45° in a broad temperature range were formulated [4]. They are called now the orthoconic antiferroelectrics, because the neighborhood smectic layers give a cone of 90°.

Financial support from the Polish Government (K.B.N) – PBS 634 and European Program 'HEMID' – TST-2001-33836.

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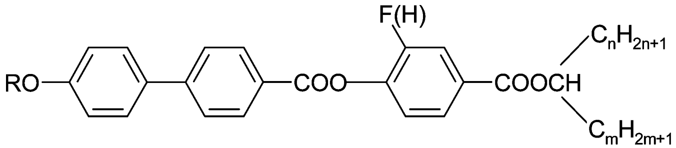
These new materials have been investigated parallel in Lagerwall's laboratory [4–7]. It was found that the orthoconic AFLC mixture is uniaxial negative liquid crystalline mixture. It behaves in normal surface stabilized cell as an isotropic medium and surface defects are not seen, what generates the excellent dark state. When this AFLC material is switched from the antiferroelectric state (AF) into one of two synclinic ferroelectric states (± F, being biaxial positive states) extremally high contrast is obtained. It seems, that these materials are the most perspective for applications among the antiferroelectric mixtures prepared until now [7] and therefore their further development is desirable. All orthoconic antiferroelectrics (AFLC) already prepared show high spontaneous polarization ($200\,\mathrm{nC/cm^2}$ or higher) and very short pitch (below $p = 1\,\mu m$) [4,8]. The material with smaller spontaneous polarization S and longer p are necessary to obtain.

Weissflog [9] as the first synthesized achiral molecules with one swallow type alkyl tail in the terminal position. We have sinthesized a similar compound [10] and found that it exhibit the smectic layer with an anticlinic order. Nishiyama, Goodby [11–13] *et al.* investigated achiral molecules with one swallow type alkyl tail in the terminal position and found many compounds with the anticlinic phase.

We decided to prepare similar structures with a fluorinated fragment in another terminal chain.

Two series of esters of the general formula were chosen to studies:



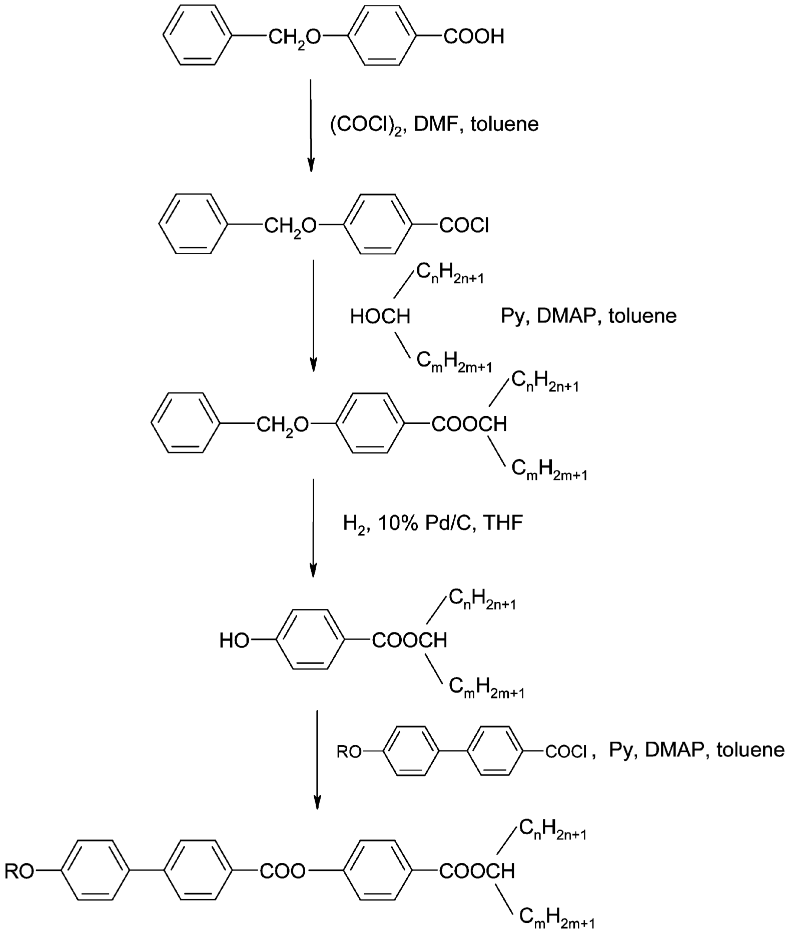
I, II

The first one (I, n = m = 3) is the achiral structure and the second one (II, n = 6, m = 1) is the chiral derivative of (S)-octanol-2, R was chosen as $C_6F_{13}C_2H_4$, $CF_3CH_2O(CH_2)_5$, $C_sF_{2s+1}COO(CH_2)_5$, $C_sH_{2s+1}COO(CH_2)_5$ group. The compounds with the spacing group $(CH_2)_5$ were prepared instead of $(CH_2)_3$ used before [8] in the aim to decrease the tendency to form a higher ordered smectic I_A phase.

The aim of presented studies was to find how the changes of different molecule units influence the mesomorphic properties of the compounds (temperatures, enthalpies and the sequence of phase transitions) and to find members with the best properties for mixture formulation.

SYNTHESIS

The used methods of syntheses of esters I and II are given in Scheme 1 in the case of R = 1H,1H,2H,2H-perfluorooctyl or 5-(1,1,1,-trifluoroethoxy)-



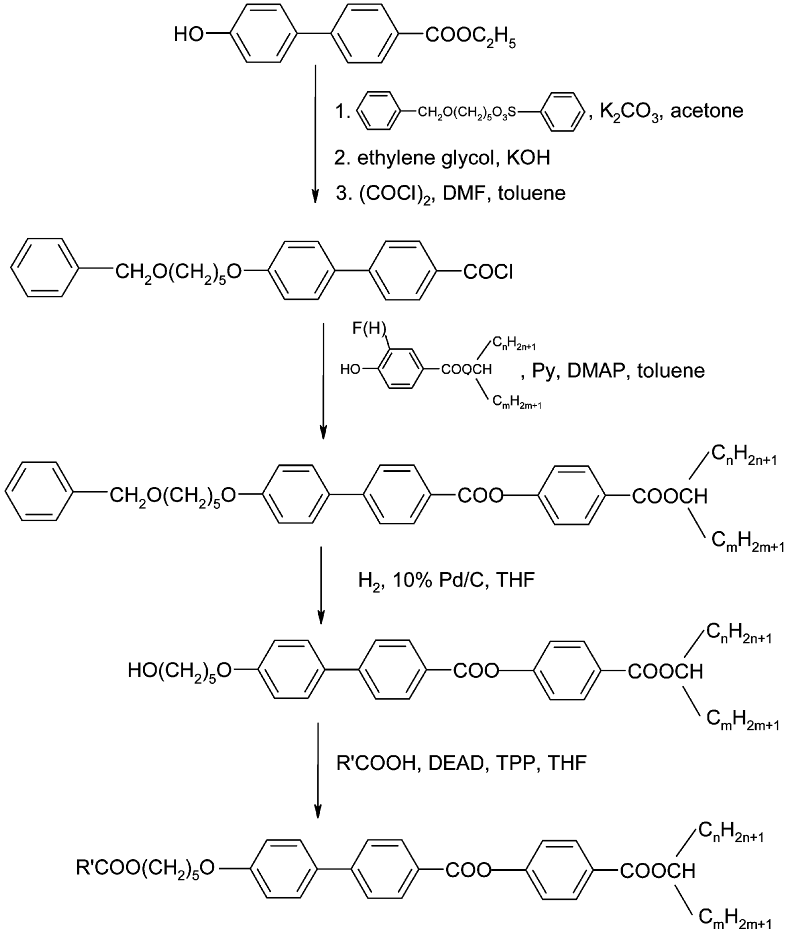
SCHEME 1 Synthetic route of eteroesters I (n = m = 3) and II (n = 6, m = 1); R = $C_6F_{13}CH_2CH_2$- or $CF_3CH_2O(CH_2)_5$-.

pentyl and in Scheme 2 in the case of R = 5-(alkanoyloxy)pentyl or 5-(perfluoroalkanoyloxy)pentyl.

The detailed description of preparative procedures and purification methods are given in earlier papers [2,14] for similar esters.

MESOMORPHIC PROPERTIES

The phase transition temperatures and enthalpies of esters I and II were measured by DSC (SETARAM 141) and were confirmed by polarizing

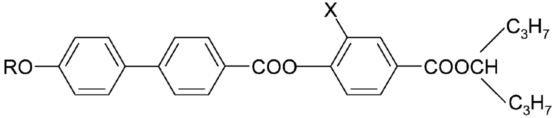


SCHEME 2 Synthetic route of triple esters I and II; $R' = C_sF_{2s+1}$- or C_sH_{2s+1}-.

microscopy observations (BIOLAR PZO connected with LINKAM TMS-91 heating stage), by the miscibility with the compounds of known phase situation and by X-ray diffraction patterns. The results of studies are summarized in Table I and II.

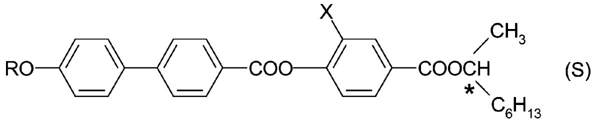
The swallow type chain esters I (derivatives of 4-heptanol) exhibit the poor number of smectic phases. The smectic A phase at higher temperature range and only a single tilted phase at lower temperature range are observed, except for the compound I.5, which has only SmA phase. The tilted phases are either the synclinic smectic C phase (SmC) or the anticlinic smectic C phase (SmC_{Anti}). The substituted esters with fluorine in the nearest benzene ring to the swallow type tail have higher melting points,

TABLE I Phase Transition Temperatures [°C] (Onset Point, Upper Line) and Heat Fusion Enthalpies [kJ/mol] (Bottom Line) for Series I as Obtained from DSC Measurement; ( ) – Monotropic Phase from Microscopic Observation



No	R	X	Cr_1		Cr		SmC_{Anti}		SmC		SmA		Iso
I.1	$C_6F_{13}C_2H_4-$	H	–		*	131.4	–		(*	76.5)	*	154.1	*
												2.89	
I.2	$CF_3CH_2O(CH_2)_5-$	H	–		*	*36.0*	–		*	100.4	*	104.1	*
						90.2							
						35.50				*1.42*		*2.55*	
I.3	$CF_3CH_2O(CH_2)_5-$	F	–		*	112.9	–		(*	68.6)	*	82.0)	*
						49.86				*0.42*		*3.10*	
I.4	$C_3H_7COO(CH_2)_5-$	H	–		*	53.7	*	71.8	–		*	76.0 *2.47*	*
						17.08		*0.75*				*2.47*	
I.5	$C_3H_7COO(CH_2)_5-$	F	–		*	68.8	–		–		(*	51.3) *	
						43.71							
I.6	$C_3F_7COO(CH_2)_5-$	H	–		*	95.8	(*	88.6)	–		*	102.6	*
						28.60		*1.84*				*1.80*	
I.7	$C_3F_7COO(CH_2)_5-$	F	*	97.1	*	102.2	(*	66.7)	–		(	74.8)	*
				4,06		*43.54*		*0.00*				*1.93*	
I.8	$C_4F_9COO(CH_2)_5-$	F	*	94.5	*	101.5	(*	69.3)	–		(*	82.0)	*
				3.81		*43.12*						*2.34*	
I.9	$C_3F_7COO(CH_2)_6-$	H	–		*	74.6	*	90.4	–		*	103.8	*
						20.68		*1.67*				*2.01*	
I.10	$C_4F_9COO(CH_2)_6-$	H	*	44.7	*	61.3	*	92.5	–		*	112.7	*
				0.96		*16.37*		*1.38*				*2.55*	

TABLE II Phase Transition Temperatures [°C] (Onset Point, Upper Line) and Heat Fusion Enthalpies [kJ/mol] (Bottom Line) for Series II; ( ) - Monotropic Phase.



No	R	X	Cr_1		Cr		SmC_{Anti}		SmC		SmA		Iso
II.1	$C_6F_{13}C_2H_4-$ [15]	H	*	80.7 *12.64*	*	98.1 *19.26*	*		*	148.1 *0.84*	*	183.6 *4.73*	*
II.2	$C_6F_{13}C_2H_4-$	F	–		*	83.4 *24.37*	*		*	134.9 *0.75*	*	155.6 *4.35*	*
II.3	$CF_3CH_2O(CH_2)_5-$	H	–		*	77.6 *28.09*	*	*126.9* *0.50*	*	127.3	*	136.6 *4.98*	*
II.4	$CF_3CH_2O(CH_2)_5-$	F	*	60.9 *7.28*	*	63.0 *27.42*	*	91.0 *0.04*	*	92.5 *0.08*	*	109.1 *5.19*	*
II.5	$C_3H_7COO(CH_2)_5-$	H	–		*	74.5 *36.76*	*	95.3 *0.42*	–		*	108.5 *3.93*	*
II.6	$C_3F_7COO(CH_2)_5-$	H	*	51.9 *8.04*	*	65.5 *19.68*	*	121.7 *0.096*	*	124.6 *1.26*	*	132.7 *3.18*	*
II.7	$C_3F_7COO(CH_2)_5-$	F	–		*	48.5 *26.21*	*	101.3 *0.13*	*	102.7 *0.96*	*	106.4 *3.85*	*
II.8	$C_4F_9COO(CH_2)_5-$	H	–		*	60.5 *40.07*	*	117.6 *0.063*	*	123.7 *1.17*	*	136.9 *3.14*	*
II.9	$C_4F_9COO(CH_2)_5-$	F	–		*	44.5 *22.73*	*	100.5 *0.063*	*	105.2 *1.13*	*	109.6 *4.14*	*

higher melting enthalpies and lower clearing points than unsubstituted analogues. Their smectic phases are only monotropic.

The chiral esters II being derivatives of octanol-2 (having less branched but longer chain than in series I) show a richer smectic polymorphism. The anticlinic (SmC_{anti}^*), synclinic (SmC^*) and orthogonal SmA phases are simultaneously observed. Here the compounds with $(CH_2)_5O$- between the fluorinated alkanoyloxy unit and the biphenyl ring have the phase sequence and the phase stability very similar as was observed in their analogues with $(CH_2)_3O$- spacing group [2]. A positive change with comparison to the latter structure is that a higher ordered SmI_A^* phase is not observed and the melting points here are decreased although slightly. In case of the series II fluoro substitution in lateral position decreases slightly the melting point and stronger the clearing point.

X-RAY MEASUREMENTS

The change of smectic layer spacing (d) for some compounds I (I.2, I.6) were measured. Their temperature dependence of the ratio d/d_A is presented in Figure 1, where the data for compounds II (II.3, II.7, II.9) are also presented for comparison.

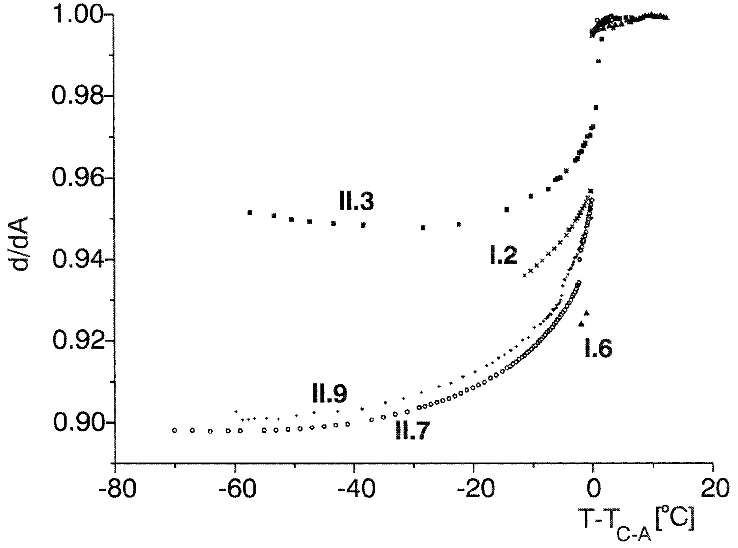


FIGURE 1 Temperature dependence of d/d_A smectic layer spacing for **I.2, I.6, II.3, II.7** and **II.9**. $T_{C\text{-}A}$ – transition temperature to a tilted phase.

A very strong drop of the layer spacing d during transition from the orthogonal smectic A phase to the tilted phase is observed. It correlated with the strong first order character of this transition as it results from the observed values of the transition enthalpy, see Table 1. This drop expressed by decreasing d/l or d/d_A ratio changes in the following order for the chains:

	$CF_3CH_2\text{-}O(CH_2)_5O\text{-}$ <	$C_3H_7COO(CH_2)_5O$ <	$C_3F_7COO(CH_2)_5O\text{-}$
d/d_Aequals	0.94	0.92	0.9

at temperatures 10 deg below the transition SmC_{Anti}-SmA. The same was recently reported for the compounds with the $(CH_2)_3$ spacer [8].

The compound I.6 has the smectic layer tilted the same high as it was found for the chiral compound with the chain $C_4F_9COO(CH_2)_3O$ or $C_3F_7COO(CH_2)_3O$ [8].

PHASE DIAGRAM AND THE INDUCTION OF AN ANTICLINIC PHASE STUDIES

Similarity in the tilt values of achiral and chiral analogues is confirmed by miscibility phase diagrams studies, Figure 2.

It is known, that the smectic C phase is destabilized and the phase border SmC-SmA decreases strongly when the compounds with different layer tilts are mixed [16]. The Figures 1a and 1b show that the achiral compound

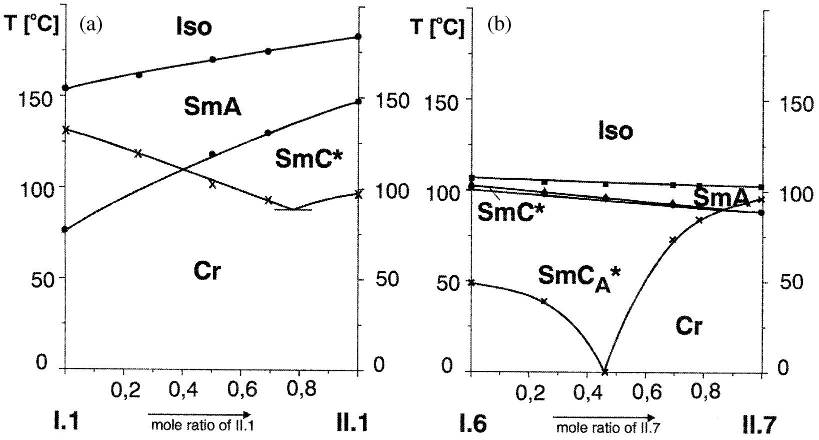


FIGURE 2 Phase diagrams of mixtures **I.1–II.1** – a and **I.6–II.7** – b, x – melting points.

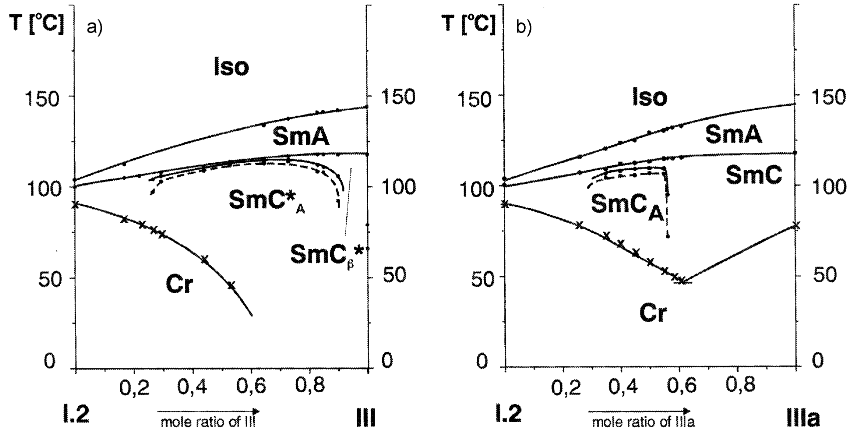
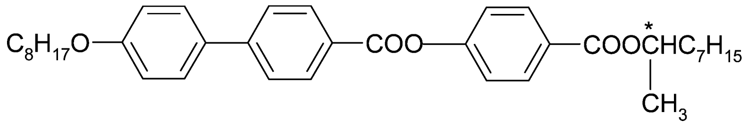


FIGURE 3 Phase diagrams of mixtures **I.2-III** – a and **I.2-IIIa** – b, x – melting points.

I.1 and chiral compounds II.1 mix themselves additively and form the simple eutectic in the solid phase, also the same behavior is observed for the pair of compounds I.6–II.7.

The achiral fluorinated compound I.2 exhibiting only the synclinic SmC and orthogonal SmA phase is able to induce anticlinic smectic C$_A$* phase, when is mixed with chiral protonated compounds, for example compound III, as well as its racemic (R, S) form compound IIIa, see Figures 3a, b.



III

Phase transition
Cr$_1$ 60.8 Cr 79.6 (SmI$_A$* 65.8) SmC$_\beta$* 118.6 Sm$_\alpha$ 119.6 SmA 144.1 I (S) [17]
Cr 79 (SmI$_A$* 65.8) SmC$_\beta$* 118.6 Sm$_\alpha$ 119.6 SmA 144.1 I (S,R) [17]

CONCLUSION

Achiral esters I with a swallow type terminal chain such as arised from 4-heptanol and having a fluorinated part in another chain may form a high tilted smectic phase with the synclinic or anticlinic layering. Therefore they can be used as the components of orthoconic mixtures decreasing their spontaneous polarization and elongating the helical pitch.

The lateral substitution by a fluorine atom of the rigid core of ester molecule is not convenient in the case of strongly branched esters, because it produces mesogenes with high melting points and high melting enthalpies, but may be recommended for molecules with less branched and longer tails. It is possible to induce smectic anticlinic phase ($\mathrm{SmC_{Anti}}$), when the synclinic achiral esters (SmC) are mixed with other sinclinic ester which molecules are chiral or racemic.

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