

Miscibility studies of disc-like molecules

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Abstract. The total miscibility method is applied to study the recently discovered mesophases of disc-like molecules, benzene-hexa-*n*-alkanoates. These compounds do not form continuous solid solutions, but are totally miscible in the liquid and mesomorphic states. The virtual mesophase-isotropic transition temperature for the hexanoate compound derived from the miscibility diagram is in excellent accord with that obtained from the previously reported pressure-temperature phase diagram. With simplifying assumptions, it is possible to predict with acceptable reliability the isobaric binary phase diagrams of any two members of the series. The real and virtual mesophase-liquid transition temperatures are linear functions of the molecular weight. On the other hand, a plot of the crystal-liquid transition temperatures versus the molecular weight exhibits a minimum. Total miscibility in the mesomorphic state is not observed for two members of different discogenic series, but the existence of different mesophase types is not proved. Lyotropic mesomorphism for a disc-like mesophase is established.

Keywords. Liquid crystals; disc-like molecules; miscibility; phase diagram; benzene-hexa-*n*-alkanoates; triphenylene-hexa-*n*-ethers; triphenylene-hexa-*n*-alkanoates.

1. Introduction

Since 1959 the total miscibility method (Arnold and Sackmann 1959) has been used extensively to identify mesophases of rod-like molecules (or what may be termed as *calamitic* mesophases, Billard *et al* 1978). In many cases (Malthête *et al* 1971, 1973; Domon and Billard 1973) the isobaric phase diagrams for the mixtures can be calculated from the thermodynamic data for the pure components using the formulae of Le Chatelier (1885) and Van Léar (1908). With the discovery of thermotropic mesophases in pure compounds consisting of disc-like molecules—benzene-hexa-*n*-alkanoates (hereafter abbreviated to BHA; Chandrasekhar *et al* 1977, 1979), triphenylene 2, 3, 6, 7, 10, 11 hexa-*n*-ethers (hereafter abbreviated to THE; Dubois 1978; Billard *et al* 1978, Destrade *et al* 1979), triphenylene 2, 3, 6, 7, 10, 11 hexa-*n*-alkanoates (hereafter abbreviated to THA; Destrade *et al* 1979)—it is of interest to apply this method to the *discotic* mesophases as well (Dubois 1978; Billard *et al* 1978). We present here some results relating to binary phase diagrams of mixtures of the BHA series of compounds amongst themselves and with other disc-like molecules.

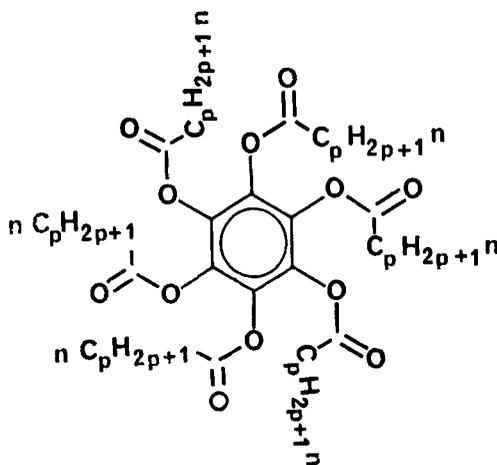
It may be remarked that the structures of these discotic phases are quite different from those of the calamitic phases. From optical and x-ray studies of BHA, Chandrasekhar *et al* (1977) proposed a structure in which the discs are stacked in columns and are irregularly spaced, the different columns forming a regular

hexagonal array. The x-ray observations of Levelut (1979) on THE (particularly the pentyl derivative) confirm the model of Chandrasekhar *et al* (1977) except that the molecules now have a larger rigid core, and the monodomain patterns reveal a partially ordered stacking of the core as distinct from a more liquid-like disorder of the chains.

2. Materials and textures

The compounds chiefly studied here are the BHA series reported by Chandrasekhar *et al* (1977, 1979), the thermodynamic data for which are presented in table 1. The

Table 1. Temperatures and heats of transitions for the BHA compounds



p	K_2	K_1	D	L
5	75.7 3.8	.	.	94.5 7.9 (89)*
6	.	80.5 7.6	.	86.1 * 5.3
7	.	79.8 10.7	.	83.7 4.5
8	.	.	.	80.5 16.7 (78.7)** 3.4

The phases exhibited by a compound (solid K , disc-like mesophase D and liquid L) are indicated by a point in the corresponding column. The transition temperatures were obtained on heating and are given in °C and the transition molar enthalpies in kcal/mole.

*virtual transition temperature obtained by extrapolating the transition line in a phase diagram.

**transition temperature obtained on reheating the monotropic mesophase.

virtual mesophase-isotropic transition for the hexanoate ($p=5$) is obtained from an extrapolation of the transition line in a phase diagram (see below).

The mesophases are very viscous and birefringent. Photographs of some optical textures have been published earlier (Chandrasekhar *et al* 1977, 1979). The melting of a single crystal needle gives a mesophase having many defects with rectilinear axes, similar to those observed by Billard *et al* (1978), parallel to the original needle axis. A relaxation of the defects appears only 0.5°C below the clearing temperature. By cooling from the liquid state, mesophase domains appear without digitation (see Billard *et al* 1978); the growth speed is highly anisotropic and occurs practically in only one direction. Many defects are found with rectilinear axes parallel to the highest growth speed direction. These defects appear even at a cooling rate of $0.2^{\circ}\text{C}/\text{min}$. The crystallisation gives elongated and birefringent crystals, sometimes curved, and there is no regularity in the angles between them.

3. Isobaric binary phase diagrams for similar disc-like molecules

The binary phase diagrams at atmospheric pressure were obtained by observation of contact preparations (see Kofler and Kofler 1954) through a polarising microscope (Leitz, Panphot) equipped with a heating stage (Mettler, F.P.5). The observed enantiotropic transitions are presented as solid lines in figures 1 to 4. The dotted lines in figures 2 and 3 correspond to observed monotropic transitions.

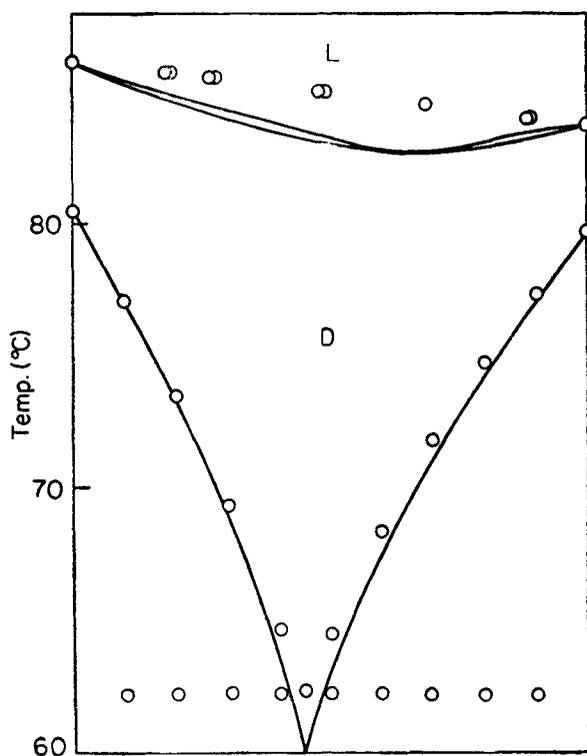


Figure 1. Isobaric phase diagram for the mixtures of BHA compounds $p = 6$ (on the left) and $p = 7$ (on the right) (table 1).

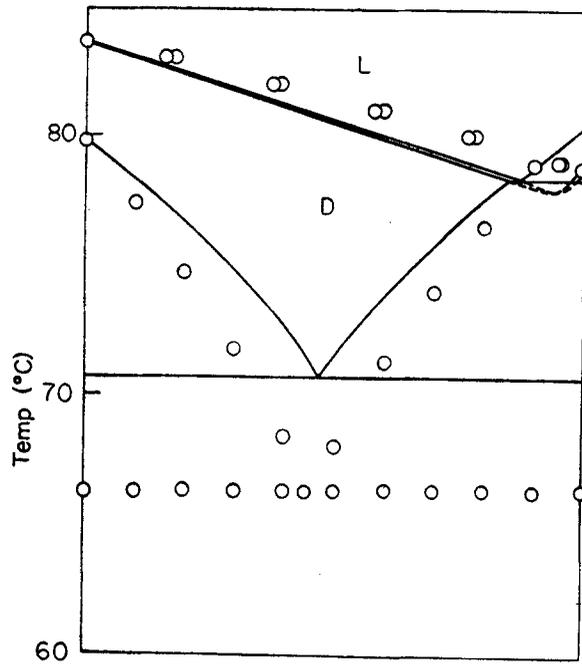


Figure 2. Isobaric phase diagram for the mixtures of BHA compounds $p = 7$ (on the left) and $p = 8$ (on the right) (table 1).

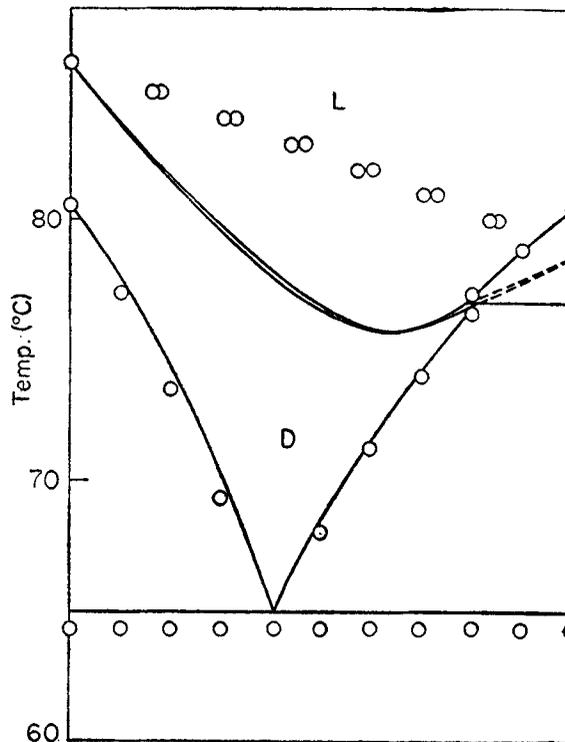


Figure 3. Isobaric phase diagram for the mixtures of BHA compounds $p = 6$ (on the left) and $p = 8$ (on the right) (table 1).

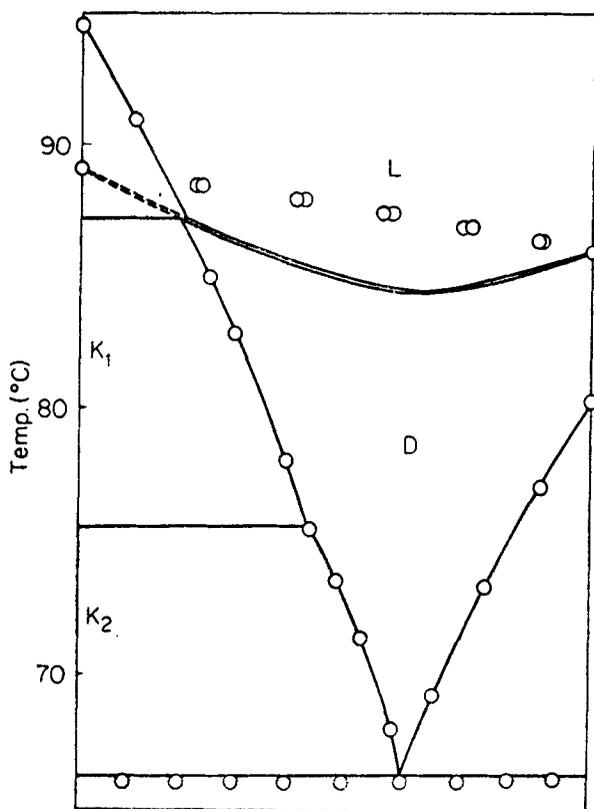


Figure 4. Isobaric phase diagram for the mixtures of BHA compounds $p = 5$ (on the left) and $p = 6$ (on the right) (table 1)

The dotted lines in figure 4 are the extrapolation of the observed spindle for the enantiotropic mesophase-liquid transition. This yields a virtual mesophase-liquid transition at 89°C for the hexanoate ($p=5$, see table 1). The pressure-temperature phase diagram for the same compound has been investigated by Shashidhar and Venkatesh (see figure 8 of Chandrasekhar *et al* 1979). The compound, which is normally non-mesomorphic, becomes enantiotropic mesomorphic above 0.16 kbar, the crystal-mesophase-isotropic triple point being at 94.9°C , 0.16 kbar. The extrapolation of this mesophase-liquid transition line to atmospheric pressure leads to a virtual, monotropic, transition at 89.1°C , in excellent accord with that obtained from the miscibility diagram (figure 4). The supercooled liquid phase can be observed down to 88.3°C , but it is possible that there is considerable delay in the liquid-mesophase monotropic transition and therefore was not observed.

Though these compounds are similar they do not form solid solutions. However, in all cases, they are totally miscible, in pairs, in the liquid and mesogenic states. The spindles exhibit minima, showing that the two solutions are not perfect (Domon and Billard 1973). However, with the usual simplifying assumptions (Malthète *et al* 1973), viz., that the liquid and mesomorphic solutions are perfect, there is no miscibility in the solid state, the heat capacities at constant pressure for the different states are equal for a given compound, the calculations with the measured data for the pure components (Malthète *et al* 1973; Domon and Billard 1973) (the circles in figures

1 to 3), give eutectic temperatures, which are in reasonable agreement with the observed values (table 2).

The enthalpy of the virtual mesophase-liquid transition is not available for the hexanoate ($p=5$) to enable one to calculate the phase diagram for this compound (figure 4). However, since the observed temperatures for the eutectic point (66.3°C) and the liquid-mesophase-crystal K_1 triple point (87.25°C , see figure 4) are known, it is possible to calculate the phase diagram completely. This is represented by circles in figure 4.

The calculated spindles (circles in figures 1 to 4) exhibit slight curvatures in the opposite sense to those of the observed spindles. But the differences between the calculated and observed temperatures (table 2) are not too large, the maximum difference being for the case for which there is greater difference between the components.

Similar results are obtained for the THE series (table 3, Dubois 1978; Billard *et al* 1978; Destrade *et al* 1979) as well as for the THA series (table 4, Destrade *et al* 1979).

Table 2. Differences between the observed and calculated values for the binary phase diagrams of the BHA compounds

Figure	Components p (see table 1)	Eutectic temperatures ($^{\circ}\text{C}$)			Maximum differences between the observed and calculated clearing temperatures ($^{\circ}\text{C}$)
		Observed	Calculated	Difference	
1	6 — 7	60.0	62.2	-2.2	-2.0
2	7 — 8	70.7	66.3	+4.4	-1.2
3	6 — 8	65.0	64.3	+0.7	-6.0
4	5 — 6	66.3			-3.0

Table 3. Differences between the observed and calculated values for the binary phase diagrams of the THE compounds

Components (numbers of carbons in the aliphatic chains)	Reference	Eutectic temperatures ($^{\circ}\text{C}$)			Maximum differences between the observed and calculated clearing temperatures ($^{\circ}\text{C}$)
		Observed	Calculated	Difference	
5 — 7	2	55	54	1	-12
6 — 8	12	50	55	-5	-18
6 — 10	12	55	52*	3	no total miscibility

*For equilibrium with the liquid phase.

Table 4. Differences between the observed and calculated values for the binary phase diagrams of the THA compounds

Components (numbers of carbons in the aliphatic chains)	Eutectic temperatures ($^{\circ}\text{C}$)			Maximum differences between the observed and calculated clearing temperatures ($^{\circ}\text{C}$)
	Observed	Calculated	Difference	
7 — 9	30	50	-20	-10
9 — 10	60	57	3	-7

It is worth mentioning that there are several instances of rod-like mesogens giving rise to binary phase diagrams with curved spindles (Domon and Billard 1979). Figure 5 is an example of a phase diagram for two very similar isometric smectogens (Malthête *et al* 1976).

The results reported here prove that simple thermodynamical calculations can give, for chemically similar disc-like mesogens, predictions with an accuracy comparable to those obtained for calamitic mesogens.

If one makes the simplifying assumptions mentioned earlier, the solid-liquid enthalpy and entropy changes are equal to the sums of the corresponding quantities for the solid-mesophase and mesophase-liquid transitions. The values calculated in this manner for BHA series are given in figure 6. The mesophase-liquid transition temperature is, to $\pm 1^\circ\text{C}$, a decreasing linear function of the number p of aliphatic carbons in the side chains. Stable mesophases appear for the heptanoate and octanoate ($p=6$ and 7) because the crystal-liquid transition temperature exhibits a minimum. For the crystal-liquid enthalpy changes, the deviations from linearity are up to 10%.

4. Other phase diagrams

We shall now consider mixtures of dissimilar molecules. It has been observed that two THE compounds with different chain length (hexyloxy and decyloxy) are not

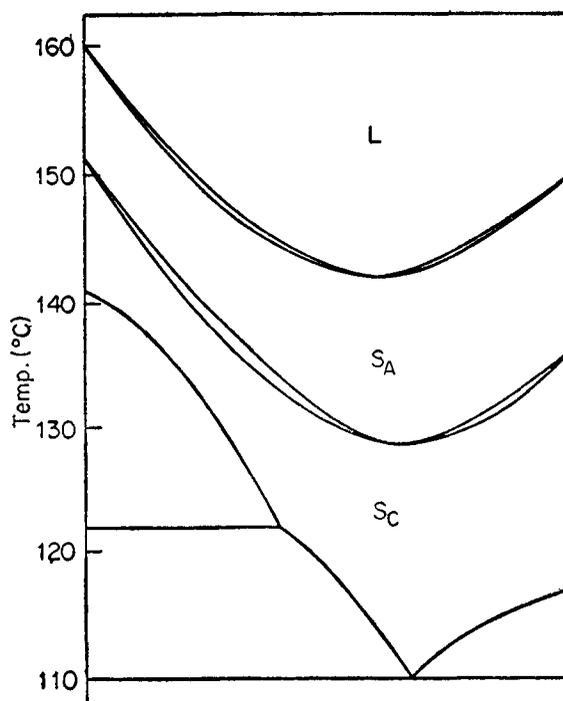


Figure 5. Isobaric phase diagram for the mixtures of 2,7-di-*n*-heptanoylfluorene (on the left) and 2-hexanoyl-7-octanoylfluorene (on the right). (Canceil *et al* 1973, 1975)

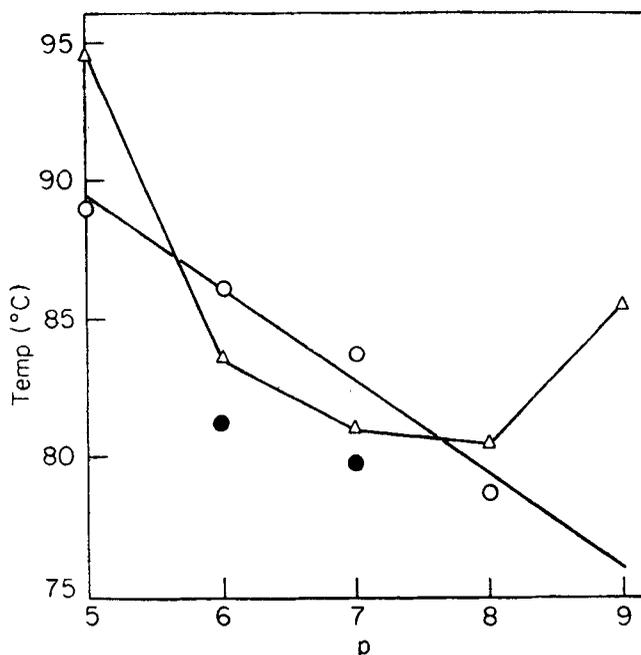


Figure 6. Transition temperatures of the BHA compounds versus the number p (table 1): Δ crystal-liquid, \bullet crystal-mesophase and \circ mesophase-liquid transitions.

continuously miscible in a mesophase (Destrade *et al* 1979). For this reason, we first carried out miscibility studies with THE and BHA compounds having similar dimensions. However, total miscibility is not observed in the mesophase. For example, for the mixture of THE ($p=7$) and BHA ($p'=8$), the liquid is in equilibrium with a mesophase and the BHA crystals at 65°C . For $p=5$ and $p'=6$, the liquid is in equilibrium with BHA crystals and with a mesophase isomorphic with that of THE at $T_2=73^\circ\text{C}$, and with a mesophase isomorphic with that of BHA at $T_1=80^\circ\text{C}$. (We may add here that THA (decanoate) and THE (octyloxy) do not exhibit total miscibility in the mesomorphic state, Destrade *et al* 1979).

We then studied mixtures of BHA (p') and THA (p). With $p'=8$ and $p=7$ total miscibility in the mesophase is not observed. It should be emphasised, however, that in all the hypomesogenic (Domon and Billard 1973) phase diagrams reported here, there does not exist an equilibrium between mesophases, and thus we have no proof of the existence of different mesophase types in the three series.

The mesophase formed by the mixtures of BHA ($p=5$) with benzene has been described previously by Madhusudana and Kumar (see Chandrasekhar *et al* 1979). In the phase diagram (figure 7), a stable mesophase appears between the crystal and the liquid only between 56 and 79.5°C . The dotted curve in figure 7 is an extrapolation to the virtual mesophase-liquid transition of the pure ester. The circles represent the calculated values. The stability field for the mesophase is very narrow. The mesophase is easily supercooled, and the crystallisation process is difficult. This fact explains the previously reported observations made with evaporation at room temperature. This is the first example of lyotropic mesomorphism for a disc-like mesophase.

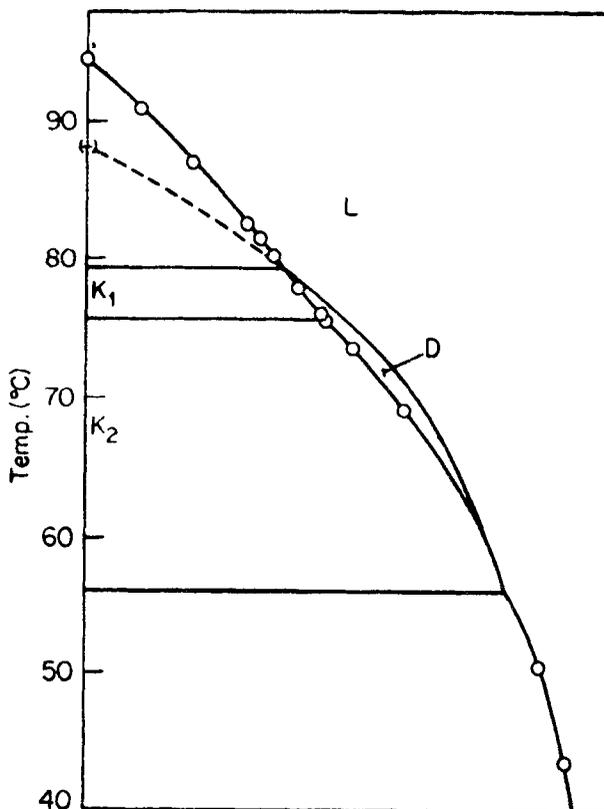


Figure 7. Phase diagram of the mixtures on the BHA compound $p = 5$ (on the left) and benzene (on the right).

Having observed an elevation of the mesogenic properties due to a disc-like solvent similar to the core, we then tested the miscibility of BHA with a solvent similar to the side chains. The phase diagram for the mixtures of BHA ($p=6$) with normal undecan is hypomesogenic with a crystal-mesophase-liquid triple point at 77.5°C . The elevation effect observed with benzene as the solvent does not occur in this case.

5. Conclusion

With the total miscibility method, the isomorphism of the disc-like mesophases formed by the BHA series of compounds (Chandrasekhar *et al* 1977, 1979) is established. From the isobaric binary phase diagram a virtual mesophase-liquid transition is found at 89°C for the hexanoate ($p=5$), in excellent agreement with that derived from the temperature-pressure phase diagram (Chandrasekhar *et al* 1979). The usual simple assumptions (Malthète *et al* 1973, Domon and Billard 1973) suffice to predict, with acceptable reliability, the isobaric binary phase diagrams of the disc-like mesogens of a given series.

Plotted against the molecular weight the mesophase-liquid virtual and real transition temperatures of the BHA series exhibit a linear decreasing trend, while the crystal-liquid transition temperatures exhibit a minimum for $p=8$.

Total miscibility in a mesophase has not so far been found for two components belonging to two different discogenic series. However, since equilibrium between two mesophases is not observed, the existence of different mesophase types in the three series is not proved.

In the phase diagram of the mixtures of BHA ($p=5$) with benzene, a stable disc-like mesophase appears. This is the first example of lyotropic mesomorphism for a disc-like mesogen.

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